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# **Environmental Analysis of U.S. Navy Submarine Solid Waste Discharges**

**Report of Findings**

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## EXECUTIVE SUMMARY

International regulations negotiated through the International Maritime Organization (IMO) have imposed restrictions pertaining to pollution from vessels in international waters. Regulation 5 of Annex V to the International Convention for the Prevention of Pollution from Ships, 1973, as modified by the Protocol of 1978 (MARPOL 73/78) prohibits the discharge of non-food solid wastes into oceanographic and ecological areas, known as Special Areas. These Special Areas include the Baltic Sea, the North Sea, the Mediterranean Sea, the Wider Caribbean Region (including the Gulf of Mexico and the Caribbean Sea), the Antarctic area, the Black Sea, the Red Sea, and the "Gulfs" area (including the Persian Gulf and the Gulf of Oman). Currently, only the North Sea, the Baltic Sea, and the Antarctic areas are in force.

The U.S. Congress, through provisions of the Marine Plastic Pollution Research and Control Act (MPPRC) of 1987 and the National Defense Authorization Act for Fiscal Year 1994 (DAA-94), required that the U.S. Navy come into full compliance with MARPOL 73/78. The provisions called for compliance of all U.S. Navy surface ships in all enforced Special Areas by December 31, 2000, and for submarines by December 31, 2008. Subsequently, the National Defense Authorization Act for Fiscal Year 1997 (DAA-97) modified the law to allow for the discharge of processed solid waste from Navy in Special Areas.

DAA-94 required the Navy to submit to Congress a plan for vessel compliance with MARPOL Annex V. The Navy submitted its' Report to Congress for surface ship compliance and is currently preparing a similar report for submarines. As part of this effort, the Naval Command, Control and Ocean Surveillance Center (NCCOSC) RDT&E Division Code D36 was tasked by the Naval Sea Systems Command (NAVSEA 03R16) to perform an environmental analysis of submarine trash disposal unit (TDU) discharges, specifically compacted paper, cardboard, metal, glass and oily paper towels. The objective of this study was to determine to what extent, if any, Navy solid waste discharges lead to adverse marine environmental effects. This report presents findings for the characterization of the submarine waste and their expected fate and effects in MARPOL Special Areas.

The study involved a review of pertinent literature, characterization of the waste stream, and field tests. The literature review focused on the regulatory framework of Special Areas, their environmental characteristics, the bulk waste stream constituents, and U.S. Navy submarine operational parameters. The waste stream characterization included physical, chemical, and biological assays as well as degradation and corrosion studies. Field tests were conducted to measure settling velocity and bottom impacts of TDU cans. The material discharged was characterized with regards to its potential for biological impacts and the operational and receiving environments were characterized to determine the likely exposures. The study was approached primarily from a theoretical standpoint, including results of previous analysis of surface ship solid waste discharges (Chadwick et al., 1996) for similar waste stream components and present analysis on new components. The analysis was approached for two spatial and temporal scales including a local scale, or single ship daily discharge case, and a basin-wide longer term assessment that considered Special Areas as a whole. Water column and sea floor processes were addressed in both cases.

The main question addressed in this study is whether the Navy's proposed TDU discharges will have an environmental impact in MARPOL Special Areas. These discharges have occurred since

World War II without evidence of significant adverse ecological effects. The findings of this study indicate that the discharged TDU cans as proposed will have no significant environmental consequences on a local or basin-wide scale in Special Areas. The fact that oceanographic conditions of Special Areas span those found in the open ocean and that the density of submarine discharges in the open ocean is less than that of Special Areas, indicates that the submarine discharges will also have no significant environmental impacts in the open ocean. The following key findings are the basis for these conclusions:

### Key Findings

- TDU containers are made of flat, precut sheet metal stock that is rolled onboard into cylinders held together with interlocking tabs. The cylinders hold approximately 25 L of compacted material with a footprint of 1400 cm<sup>2</sup>. The total weight of the cans, including the waste contents and ballasting weights, ranges between 25.6 and 29.0 kg. The sides have weep holes to allow liquid residue to run out and water to quickly penetrate the can in order to ensure that they will sink.
- The TDU wastes are comprised of organic and inorganic material in approximately equal proportions. The organic material is in the form of compacted paper and cardboard (43% by weight), which is approximately 95% cellulose. The inorganic components include waste metal (21%), steel weights (18% using two weights per can), glass (7%), and the metal TDU can itself (7%). Oily paper towels, generated primarily from the clean up of lubricating oil, are an additional 4% of the waste stream. The combined elemental constituents of the waste stream are found in quantities similar to those found in background sediments with the exception of iron, tin, and organic carbon.
- The organic material, composed mostly of organic carbon in the form of cellulose, contains little in the way of additional nutrients. Compared to typical background organic matter, the material is a poor food source and will not significantly lead to enhanced production or contribute to eutrophication.
- The discharged material contains no pollutants that would be expected to produce adverse impacts in the marine environment. A 126 priority pollutant scan consistently showed zinc at levels that are below those of concern for either sediment or water-quality criteria. Other contaminants measured in individual samples included copper, phthalate esters, and phenol. The presence of copper was considered an anomalous source for TDU cans in general. The observed levels of phthalates would be diluted by surrounding seawater to levels below those of potential concern within approximately 15 cm of the container, using conservative estimates of dilution. It is estimated that even the anomalous copper contaminant would be diluted to levels below those considered to be of ecological concern within 70 cm of the container.
- The discharged TDU cans sink rapidly at 133 m·min<sup>-1</sup> through the water column indicating that the waste will have minimal impact in the water column. Based on measured sink rates and estimates of shoreward transport in Special Areas, it is unlikely that the material will be a source of coastal litter if the cans are discharged outside the limits of 12 (water depths > 1829 m) or 25 nmi (all water depths) currently imposed by OPNAVINST 5090.1B. As a result of discharge restrictions, the containers are more likely to find their way into deep-water environments rather than shallow water areas that tend to have more sensitive biological endpoints.



- The ultimate fate of the TDU waste stream is deposition, degradation, corrosion, and burial on the sea floor. Because of highly variable rates, degradation of the paper/cardboard and corrosion of the metal is likely to occur over a period of a few years to hundreds of years. Each process will lead to a change in the aesthetic nature of the waste stream from a component of litter to a component more typical of sedimentary materials. The time scales for burial and redistribution of metal and glass waste on the sea floor can be relatively long, up to hundreds of years for complete burial and degradation. The TDU containers tested did not break open on impact with a hard, sandy bottom, indicating that the package will likely remain intact on the sea floor while it degrades.
- Seawater leaching of the TDU can material was shown to have some effects under laboratory conditions. The most sensitive endpoints in these tests indicated that a leachate concentration of about 4% caused an inhibition of growth or light production (measures of stress) on two phytoplankton species regardless of whether or not oily paper towels were present. An estimated no-effects concentration of 0.4% was predicted to occur within 122 cm of the container surface from dilution with surrounding seawater.
- In an attempt to relate toxicity results to real-world conditions, TDU cans were placed in San Diego Bay and allowed to soak for 24 hours. Seawater samples taken from inside the can showed a 15-fold lower toxic response to the most sensitive test organism than the comparable laboratory result. Seawater sampled from a distance of 50 cm away from the TDU cans showed no toxicity to the most sensitive test organism. The results indicate that a no effects concentration would be reached at a maximum of 13 cm away from the can surface. These results considered along with the observation that TDU cans placed in the Bay were colonized by a number of indigenous species, suggests that any toxicity associated with the waste materials would cause no significant impacts.
- Solid waste discharges from submarines were estimated to have no significant impact on coral reef systems. Because some physical damage to the benthos may occur upon the container's initial impact with the bottom, the potential for damage to particularly sensitive benthic species such as coral reefs was addressed. Distance-from-shore restrictions make the overlap between submarine operations and sensitive coral reef habitat unlikely. The rapid settling and limited lateral transport of TDU cans further minimizes the likelihood of their reaching regions of sensitive habitat.
- The likelihood of impact to listed threatened and endangered species is considered very low. There are only a few listed endangered and threatened species residing in MARPOL Special Areas which display feeding behaviors which could place them at risk for ingestion of submarine TDU wastes. These include five turtle species and the gray whale. It is expected that the discharge limits, the extremely low spatial density of TDU cans on the sea floor, the burial of waste by natural sedimentation processes, and the deterioration of the waste materials due to corrosion and degradation will all serve to minimize the likelihood of exposure to all threatened and endangered species.
- Solid waste mass loading from submarine operations on a basin-wide scale was assessed in this study with the goal of providing perspective on the relative contribution of discharges and their potential for impacts in Special Areas. From a perspective of sea floor coverage, the amount of surface area covered annually by TDU cans ranges up to a maximum of 0.0000004% for Special Areas, assuming no degradation of the contents. This represents only a 6% incremental coverage by submarine discharges relative to the surface fleet. Based

on annual inputs, it would take between roughly 2.6 and 46 million years to cover just 1% of the sea floor of Special Areas with submarine solid waste discharges. The calculation of these times do not take into account the slow "disappearance" of the material from the processes of degradation, corrosion, and burial. Due to the minuscule relative loading, the basin-wide impact on sea floor processes such as oxygen depletion or eutrophication is inconsequential. From a basin-wide perspective, the discharge of the submarine solid waste in Special Areas should have no adverse environmental impact.

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## ACRONYMS

ARG	Amphibious Ready Group
BG	Battle Group
BOD	Biochemical Oxygen Demand
CD/NSWC	Naval Surface Warfare Center/Carderock Division
C:N:P	Ratio of Carbon to Nitrogen to Phosphorous
COD	Chemical Oxygen Demand
COMNAVSEASYSKOM	Commander, Naval Sea Systems Command
COMSUBPAC	Commander Submarine Force, U.S. Pacific Fleet
COMSUBLANT	Commander Submarine Force, U.S. Atlantic Fleet
DCM	Deep Chlorophyll Maximum
DOC	Dissolved Organic Carbon
EC <sub>50</sub>	A Concentration Which Affects 50% of Test Organisms
ECLAC	Economic Commission for Latin America and the Caribbean
EDS	Energy Dispersive X-Ray Spectroscopy
EPA	Environmental Protection Agency
ERL	Effects Range Low
IC <sub>50</sub>	A Concentration Which Inhibits 50% of Test Organisms
ICES	International Council for the Exploration of the Seas
ICP	Inductively Coupled Plasma
IMCO	International Maritime Consultative Organization
IMO	International Maritime Organization
LC <sub>50</sub>	A Concentration Which is Lethal to 50% of Test Organisms
LOEC	Lowest Observable Effects Concentration
MED POL	Convention for the Protection of the Mediterranean Sea
MEPC	Marine Environment Protection Committee
mpy	mil per year
MPPRCA	Marine Plastic Pollution Research and Control Act
NAVSEA	Naval Sea Systems Command
NCCOSC	Naval Command, Control and Ocean Surveillance Center
NMFS	National Marine Fisheries Service
NNS	Newport News Shipbuilding
NOEC	No Observable Effects Concentration
NRaD	Naval Command, Control and Ocean Surveillance Center Research, Development, Test and Evaluation Division
ONR	Office of Naval Research
POC	Particulate Organic Carbon
psu	Practical Salinity Units
RV	Research Vessel
SEM	Scanning Electron Microscopy
TDU	Trash Disposal Unit
TOC	Total Organic Carbon
TS	Total Solids
TSS	Total Suspended Solids
UNEP	United Nations Environmental Program
WQC	Water Quality Criteria



## **1.0 INTRODUCTION**

International regulations, as specified in Annex V to the International Convention for the Prevention of Pollution from Ships, 1973, and modified by the Protocol of 1978 (MARPOL 73/78), restrict the discharge of solid wastes from ships in specific ocean areas. These MARPOL Special Areas have been negotiated through the International Maritime Organization (IMO) and include the Baltic Sea, the North Sea, the Mediterranean Sea, the Wider Caribbean Region (including the Gulf of Mexico and the Caribbean Sea), the Antarctic area, the Black Sea, the Red Sea, and the "Gulfs" area (including the Persian Gulf and the Gulf of Oman). Although MARPOL exempts public (naval) vessels, the restrictions were mandated by U.S. legislation, requiring compliance by U.S. surface ships by the year 2000 and U.S. submarines by the year 2008. This legislation has recently been modified to allow for pulped and shredded solid waste discharges from Navy vessels in Special Areas.

The Navy has researched systems and procedures for submarines to comply with MARPOL Annex V regulations and it appears that acceptable solutions for full compliance for existing platforms may not be technologically feasible. The Navy has studied several alternative solid waste management plans, taking into account technical limitations, cost, environmental impact, operational requirements, and quality of life on submarines.. One of these alternatives includes the continued use of existing submarine solid waste processing equipment, the trash disposal unit (TDU).

This report provides an environmental analysis of submarine TDU solid waste discharges in MARPOL Special Areas. This work is sponsored by Naval Sea Systems Command (NAVSEA) 03R16 and performed by the Naval Command, Control and Ocean Surveillance Center (NCCOSC) Research, Development, Test and Evaluation Division (NRaD), Code D362. This work is part of the Navy's effort to identify submarine solid waste management technologies and practices that are environmentally sound as well as technologically and economically feasible.

### **1.1 OBJECTIVES AND SCOPE**

The objective of this study is to assess the environmental impact of non-plastic solid waste discharges in TDU cans from Navy submarines in Special Areas. In order to accomplish this, a multifaceted effort to describe and quantify the thresholds and processes relevant to understanding the short- and long-term impact of the Navy's proposed discharges was initiated, and subsequent analyses performed.

The scope of this study is limited to non-plastic and non-food solid waste from U.S. Navy submarines in internationally designated Special Areas. According to existing legislation, discharge of food wastes from submarines is allowed in Special Areas if outside of 12 nmi and plastics will be banned in all ocean areas, therefore, neither have been addressed as part of this assessment. Thus, the primary waste stream of concern for this project includes paper, cardboard, metal, glass, and oily paper towels which are compressed into cans for discharge through the submarine TDU. Also included in the waste stream will be the TDU cans themselves and the steel weights that are added to the cans to ensure sinkability. Additionally, the impact of non-corroding TDU cans will be discussed as well.

This study uses similar methodology to the NRaD fate and effects study on U.S. Navy surface ship solid waste discharges, which is documented in NCCOSC Technical Report 1716

"Environmental Analysis of U.S. Navy Shipboard Solid Waste Discharges: Report of Findings" by Chadwick et al. (1996). These findings for surface ships were incorporated in the November 1996 "Report to Congress: U.S. Navy Ship Solid Waste Management Plan for MARPOL Annex V Special Areas" and the associated "Final Environmental Impact Statement: Disposal of U.S. Navy Shipboard Solid Waste". In a like manner, this study consists primarily of theoretical environmental analyses using literature reviews, laboratory data, and selected small-scale field tests. Much of the data from literature research, chemical analysis, toxicity tests, corrosion and degradation studies, and regulatory review in the surface ship fate and effects study is applicable to this work and will be referenced when appropriate. This study will support the submarine addendum to the Navy's Report to Congress and an associated Environmental Assessment.

Throughout this report a number of assumptions are used in defining the scope of the analysis. Specific assumptions will be mentioned as appropriate and the general assumptions and specific data sources utilized are listed as follows:

- Only TDU can discharges in Special Areas are being considered in this study.
- The waste stream packaged in the TDU cans with ballasting weights includes paper, cardboard, metal, glass, and oily paper towels. Oily paper towels are primarily generated from the clean up of lubricating oil (NNS, 1996). No plastic, food, or other wastes are considered.
- Current non-plastic solid waste discharge requirements for submarines defined in the Office of the Chief of Naval Operations Instruction (OPNAVINST) 5090.1B are used in this study. These include a distance from shore restriction that states: 1) no discharge within 12 nmi of land; 2) sinkable waste greater than 12 nmi of land allowed in water depths greater than 1000 fathoms (1829 m); and 3) sinkable waste greater than 25 nmi from land allowed with no depth restriction.
- U.S. Navy submarines with a typical crew complement of 130 are considered in this analysis.
- Waste generation rates were obtained from the Newport News Shipbuilding waste management study (NNS, 1994) and oily waste rag management study (NNS, 1996).
- Data on the number of submarine patrol days within the Special Areas were obtained from Commander, Submarine Force, U.S. Pacific Fleet (COMSUBPAC) and Commander, Submarine Force, U.S. Atlantic Fleet (COMSUBLANT) for the past three years. Yearly averages were calculated from these data and will be used for mass loading estimates.

## **1.2 BACKGROUND**

Concern over the environmental degradation of marine habitats by anthropogenic activities has prompted international regulations, mandated by the U.S. Congress, which restrict and prohibit the discharge of solid waste from ships and submarines, particularly in MARPOL Special Areas. There are only three Special Areas where IMO regulations are currently in effect; these are the Baltic Sea, the North Sea, and the Antarctic area. The U.S. Navy has reevaluated its' solid waste disposal practices and proposed alternative procedures with the intention of allowing the Navy to maintain readiness without adversely affecting the quality of ocean environments in which naval vessels operate. Congress recently passed legislation to allow U.S. Navy vessels to discharge

pulped paper and cardboard and shredded metal and glass wastes in Special Areas subject to distance-from-shore restrictions.

TDU's are currently being used to handle the bulk of the solid waste and are the only disposal equipment for submarines discussed in this study. They have been used effectively in the submarine fleet since World War II. The TDU cans themselves are made of flat, precut sheet metal stock that is rolled onboard into cylinders and held with interlocking tabs. The cylinders have weep holes to allow liquid residue to run out of the container and to allow water to quickly penetrate the can and ensure that they sink. The top and bottom disks are also held in place by tabs bent into slots. The cans are compacted hydraulically, and metal weights are added to ensure sinkability.

## 2.0 CONCEPTUAL FRAMEWORK

A conceptual framework for the study is described in this section. This framework incorporates issues initially identified in Swanson et al., (1994) and from general models on ocean disposal (e.g., Csanady, 1987; Brooks et al., 1987; Charnock et al., 1994), as well as the Navy discharge plan (NAVSEA, 1993). The section is divided into two components: a statement of the problem, and a set of conceptual models that incorporate processes and scales that are important to the problem, including a description of the potential environmental issues that may arise as a result of these processes. The problem statement is similar to that of any waste stream discharged into the ocean where the general goal is to determine the probability of adverse effects. The processes that determine the outcome to the problem depend on many diverse factors, which are influenced by the interactions of the waste stream and the receiving environment. Two conceptual models have been developed for the discrete TDU can discharges in Special Area environments. These conceptual models differ as a result of the scale at which the system is considered. Local effects of discharge from a single vessel can be considerably different from the combined basin scale effects due to many vessels discharging over a long period of time. A conceptual model based on a single vessel discharge is, therefore, considered separately from a basin scale view.

### 2.1 PROBLEM STATEMENT

Our formulation of the study is based on attempts to answer questions about the potential fate and effects of the waste stream. In this regard, this study follows the principles of environmental risk assessment using a dose/response model to evaluate the environmental significance of predicted exposures. A general statement of the problem is posed as,

*To what degree, if any, do the materials discharged adversely affect the marine environment?*

This broad question requires a scientific approach that attempts to answer specific questions regarding the characteristics of the waste stream, the characteristics of the receiving environment, and the manner in which the two interact. These can be divided more specifically as follows:

#### Discharge Characteristics

1. What is being discharged?
2. How much is being discharged?
3. What are the discharge conditions?

#### Receiving Environment

1. What are the hydrographic conditions that will affect the fate of the discharge?
2. What are the biological systems and other endpoints that may be affected?

#### Interactions

1. Where does the material go?
2. How and at what rate is it dispersed?
3. How and at what level are biological systems exposed and for what duration?

Our understanding of the answer to the overall question of effects is, thus, based on the degree to which we can describe the discharge and the receiving system, and the level at which we can understand the interactions between the two. While discharge characteristics are relatively easy to define, the receiving environment of Special Areas varies widely. It is problematic to evaluate all potential outcomes of an unlimited range of receiving water conditions. Thus, this study focuses on the processes important in controlling the fate and effects of the waste streams, and the more common oceanographic and environmental conditions found within Special Areas. These dominant processes are described in the conceptual models below.

## 2.2 CONCEPTUAL MODELS

**Local Scale Model.** The local scale regime addresses relatively short-term impacts due to a single vessel or possibly a fleet of vessels operating in an area of limited spatial extent. For the TDU cans, the physical processes associated with this scale are primarily related to near-field advection, and settling, while the biological issues are governed by physical impact, local exposure, corrosion, and microbial degradation. This has parallels, for example, to the previous studies of the shredded metal/glass waste stream from U.S. Navy ships (Chadwick et al., 1996). The schematic for this localized regime is shown in figure 2-1.

The TDU cans contain compressed paper, cardboard, metal, glass, and oily paper towels that are weighted with metal weights that allow the combined waste to sink quickly as a single unit. Thus, the primary factors affecting fate of the TDU waste stream in the water column include the density and sinking characteristics of the can, the lateral transport that may occur during sinking, and short-term exposure to water-column organisms. It is anticipated that the TDU waste will reach the bottom rapidly, so that most of the processes that influence the fate and effects of the waste will occur at or near the sediment water interface. The primary fate of the material will be influenced by burial, degradation, corrosion, and possible transport by bottom currents. Potential detrimental effects include physical damage and toxicity to benthic organisms, ingestion of the waste by benthic feeders, oxygen uptake during corrosion processes, and beach and shore zone litter.

A typical scenario for the life cycle of the TDU can begins with the ejection of the waste from the submarine, containing, primarily, compressed paper, tin cans, aluminum, and glass. The cans are then transported by currents as they sink rapidly to the bottom. The lateral distance from the discharge point to bottom impact is dependent on current strength and water depth. Once the cans settle on the bottom, they will tend to stay in place except under very strong current conditions. At this point, benthic organisms may be exposed to the waste, and the hard material of the can may provide a substrate for benthic colonization. Degradation of the paper material and the corrosion of the metal TDU can and the metal components of its contents will take place. The paper materials are expected to decompose first, while the corrosion and breakdown of the TDU can and the metal/glass debris will occur over a longer time period. Eventually, much of the waste will be buried.

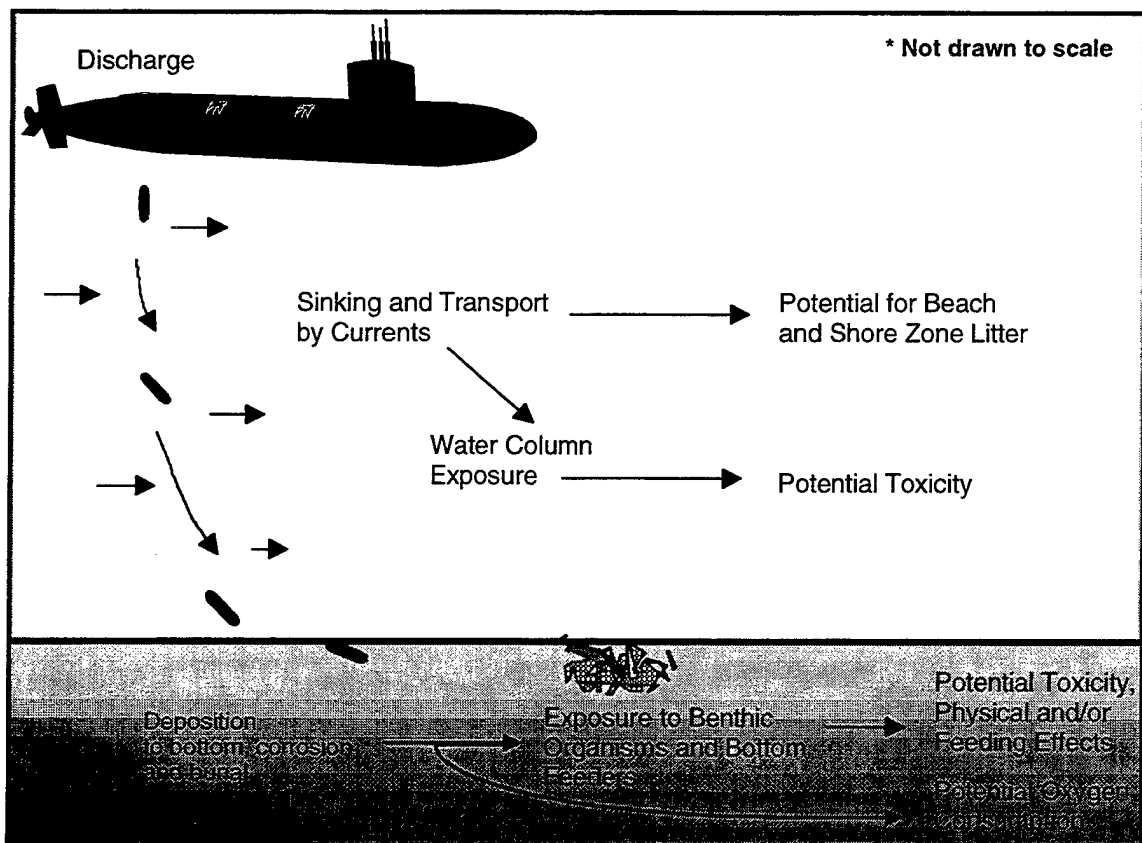


Figure 2-1. Conceptual local scale model for determining the potential fate and effects of submarine solid waste discharged in TDU containers. The wastes inside the containers include paper/cardboard, metal, glass, and oily paper towels. \*Note, diagram is not drawn to scale; TDU cans are shown relatively larger than actual.

**Basin Scale Model.** The second regime involves a larger, basin scale view of the problem. This scenario incorporates the idea of a number of vessels operating over broad spatial scales for extended periods of time. The primary processes addressed in this view include aspects of overall mass loading, sedimentation, litter, accumulation, and chronic low-level exposure. The goal of this approach is to provide a perspective on the relative contribution of vessel discharges to the overall loading of regions or basins for constituents that are present in the shipboard waste stream. The primary components of the waste stream include organic cellulose materials from the paper waste and inorganic wastes associated with metals and glass. These are compared to the basic elemental constituents in most regions from a variety of natural and anthropogenic sources, including river inflow, *in situ* biological production, domestic sewage outfalls, industrial and agricultural discharges, and ocean dumping. While the form of submarine solid wastes is significantly different from that of the other inputs, the constituents are compared with respect to their overall mass loading.

### **3.0 TECHNICAL APPROACH**

The goal of this assessment was to isolate potential pathways, endpoints, and areas of impact based on reasonably foreseeable estimates of loading, and conservative measures of physical and ecological response. The technical approach is structured into five primary steps, including an analysis of operational profiles, receiving system, waste stream characteristics, fate and effects of TDU discharges, and overall environmental analysis. Individual components are described in detail below.

#### **3.1 OPERATIONAL PROFILES**

Operational profiles for typical submarine TDU discharges were compiled from previous Navy studies and direct information requests. Two types of information were acquired, including data to estimate the typical discharge rates of TDU cans from submarines, and data to estimate the typical number of patrol days for submarines in MARPOL Special Areas. Information on, discharge rates was compiled from studies conducted and published by Newport News Shipbuilding (NNS) under contract to NAVSEA in November 1994 as part of their study on waste discharge options for the design of the new attack submarine. Information regarding number of patrol days in Special Areas was determined from direct information requests submitted to COMSUBLANT and COMSUBPAC. Operational profiles and specific assumptions for this study regarding operations are provided in section 6.0.

#### **3.2 RECEIVING SYSTEM**

Characterization of the receiving system focused on reviews of the eight MARPOL Special Areas: the Baltic Sea, Wider Caribbean Region, Mediterranean Sea, North Sea, Antarctic Area, Black Sea, Red Sea, and the Gulfs Area. While each Special Area has unique characteristics, taken together, they represent environmental conditions that span the range of conditions found in the world's oceans. The reviews (five in Chadwick et al. 1996 and three that will be included in the document's addendum) were performed to obtain background on the special oceanographic, ecological, pollution, and vessel traffic conditions in these areas. Much of the information gathered forms the basis for their inclusion as MARPOL Special Areas. For each area, an attempt was made to tabulate quantitative data of pertinent physical, chemical, and biological parameters that could be used as guides for comparing TDU discharges to background conditions or other inputs to Special Areas. It was not possible to obtain numbers for all parameters in all areas. Furthermore, because there is a high degree of variability even within a single Special Area, a "typical" or average number was used.

#### **3.3 WASTE STREAM CHARACTERISTICS**

Basic knowledge of the physical, chemical, and biological characteristics of the waste stream are essential to better understand and predict the potential fate and effects of the material when it is discharged into the environment. Physical assays were performed to predict dispersion, transport, exposure, bioavailability, and aesthetic considerations. Chemical and biological assays were performed to provide an indication of the possible effects in the environment such as oxygen depletion, eutrophication, toxicity, feeding behavior, growth rate, and reproduction. Characterization of the TDU waste stream was based on two sets of information: previous tests of component materials performed during the pulped and shredded waste stream analysis

(Chadwick et al., 1996), and direct testing of TDU cans. Eleven total TDU containers were acquired and tested for physical, chemical, and toxicological characterization. Details of the waste stream characterization are presented in section 7.0.

### 3.4 FATE AND EFFECTS OF TDU DISCHARGES

Evaluation of the potential fate and effects of the TDU waste stream, was based on the information accumulated for discharge operations, receiving systems, and waste stream characteristics. Fate of the material was assessed based on the amount of material discharged, the characteristics of the waste stream components, including metal, glass, paper products, and the TDU can itself, the projected transport of the material under a range of environmental settings, and the estimated degradation or corrosion of component materials. Potential effects were evaluated on the basis of localized impacts due to physical disturbance and toxicity, and larger scale effects due to overall mass loading. Potential effects of the TDU waste stream were also assessed on the incremental addition that TDU discharges represent with respect to overall U.S. Navy vessel inputs. Specific components of the fate and effects analysis are outlined below, and the analysis itself is presented in section 8.0.

**Settling Characteristics.** Settling velocity for the TDU waste stream was tested experimentally in San Diego Bay. A calibrated pressure sensor was used to determine the depth as a function of time. Assuming that the TDU cans remained intact an estimate of transport to the bottom was then calculated using average depths in each Special Area. Accumulation and burial have both been addressed theoretically using vessel traffic data and estimates of mass loading, as well as regional data within the Special Areas on sedimentation rates, and types, and bottom flow.

**Transport Dispersion Modeling.** Transport and dispersion of the TDU waste stream was evaluated in order to estimate typical distributions of TDU cans on the sea floor for single submarine discharges and basin-wide scales of discharge. Transport following discharge was modeled on the basis of known settling rates, and typical ambient current conditions representative of each Special Area.

**Degradation of the Paper Waste Stream.** The paper materials present in the waste stream represent a source of organic material that is subject to microbial degradation in the marine environment. The degradation of these materials was assessed in detail for the pulped waste stream discharged by surface ships. The paper waste in the case of TDU discharges is compressed within the can and discharged beneath the keel of the submerged submarine, rather than pulped and discharged into the wake. The analysis of degradation of these materials for TDU discharges, thus, utilizes the information gathered for surface ship discharges (Chadwick et al., 1996) and evaluates the differences that arise due to the distinctions in processing techniques.

**Corrosion of the Metal Waste Stream.** Corrosion of the metallic constituents of the waste stream was assessed in order to provide estimates of how long this material will persist in the environment. Since corrosion rates will vary with metal type, the elemental composition of the metal materials was characterized. Because corrosion rates vary with environmental conditions such as temperature, oxygen, etc., reasonable estimates of these parameters were identified for each Special Area. Corrosion of the metal waste was estimated using literature rates for the particular metals present in the waste stream and the likely environmental conditions to which they are exposed.



*In situ* tests of both shredded metal and glass from surface ships, and filled TDU cans were also performed to provide a qualitative assessment of longevity, corrosion, and fouling under a shallow-water coastal condition.

**Effects of the TDU Waste Streams.** Effects of concern fall under the categories of biological interaction, aesthetic degradation, habitat impairment, interference with local industry such as fisheries, and possible bioaccumulation that could endanger human health. In this study, biological effects have been tested in the laboratory and extrapolated to potential impacts in the Special Area seas. This includes both biological interaction studies that were performed previously for surface ship discharges, and additional work performed specifically on the TDU waste stream. Aesthetic concerns include litter washing up on beaches, floating garbage, and water turbidity. This has been approached from both a theoretical and experimental point of view in order to determine whether or not it is likely for this waste stream to be transported to shore, given measured sinking rates and theoretical current regimes expected in Special Areas. Habitat impairment can include effects such as eutrophication, oxygen depletion, "smothering the benthos," physical damage due to impact, and the creation of uninhabitable zones where accumulation has occurred. Interference with industries such as fisheries could occur if either the material directly harms the species of interest, or if the food web is significantly altered, leading to reduced sources of nourishment. Bioaccumulation has not been addressed here because of the unlikely potential for occurrence. An assessment of the bulk constituents, the chemical composition, and the mass loading have not warranted significant investigative effort regarding the potential for bioaccumulation, therefore, it has not been addressed.

### 3.5 ENVIRONMENTAL ANALYSIS

The main question addressed in this study is whether the Navy's proposed TDU discharges will have an environmental impact in MARPOL Special Areas. However, they have occurred since World War II, and there is no known evidence of any of these materials impacting the shore, nor is there any evidence of significant adverse ecological effects. The approach has been to quantify the discharges in terms of their physical and chemical characteristics and biological response. The analysis takes into account the existing ecological, oceanographic, geological, and industrial nature of Special Areas. The predicted fate of the waste materials is based on an analysis of how they will interact with the receiving environment, given their physical and chemical characteristics and typical conditions found in Special Areas. The short- and long-term environmental impacts from these discharges are thereby assessed by projecting theoretical, laboratory, and field data to "real-world" conditions on single vessel and basin-wide spatial scales.

## 4.0 PREVIOUS STUDY FINDINGS

Results of the fate and effect study of surface ship solid waste discharges (Chadwick et al., 1996) were used as a starting point for the investigation of submarine solid waste discharges. Some of the information gathered and results of analyses were directly applicable to submarine discharges while some were used by way of comparison. The following are the key findings of the study conducted at NRaD and funded by NAVSEA 03R16 that are directly applicable to submarine discharges. There are few studies to be found that relate directly because of the unique nature of the waste stream, however, an overview of general ocean discharge studies can be found in the previous surface ship solid waste discharge report (Chadwick et al., 1996).

### 4.1 KEY FINDINGS OF THE PULPED PAPER AND CARDBOARD WASTE STREAM

- Paper and cardboard are organic material that is composed mostly of cellulose. When pulped, the material was measured to be approximately 0.3% solids by weight, of which approximately 92% is organic matter, and is low in nutrients compared to background organic matter. All of this indicates that the material will not be a significant source of nutrients in the water column or the benthos, and will most likely be avoided as a food source. Productivity should not be significantly enhanced and eutrophication should not be a major factor, however, microbial degradation may be hindered in nutrient-limited ocean areas.
- The material contains no significant amounts of toxic chemicals. A 126 priority pollutant scan showed no pollutants at levels that would be expected to produce impacts and only trace amounts of zinc ( $6 \text{ mg}\cdot\text{kg}^{-1}$ ), acetone ( $2 \text{ mg}\cdot\text{kg}^{-1}$ ), and aliphatic hydrocarbons ( $6 \text{ mg}\cdot\text{kg}^{-1}$ ), which are well below threshold levels of concern for standard sediment criteria.
- The potential impacts on water column and benthic biota tested occur only at concentrations significantly greater than would be found after discharge. Biological interactions tested with a large range of organisms from bacteria to small fish showed that the most sensitive response occurred in filter-feeding sardines causing a temporary feeding interference effect at concentrations from  $1 \text{ to } 3 \text{ mg}\cdot\text{L}^{-1}$ , or 5 to 15 times higher than found in the wake dilution. No biological effects were observed in any organism tested at concentration levels expected in the water column with wake dilution based on both particle and water phase testing. No biological effects were observed in two benthic organisms tested at concentration levels that would be expected in the sediments after 1000 ships had passed over the same location.
- Mass loading on an annual basis from regional and basin-wide Naval operations is a minuscule fraction of other coastal inputs in Special Areas. Based on an operational scenario with an Amphibious Ready Group (ARG) and a Battle Group (BG) deployed for six months in a  $10,000 \text{ nm}^2$  area, the accumulated concentrations are well below those causing biological effects.

### 4.2 KEY FINDINGS OF THE METAL AND GLASS WASTE STREAM

- The material is mostly composed of tin-coated steel cans (71% by weight) and glass (13% by weight). Minor components include aluminum cans, burlap bags, food waste, and paper labels. The elemental constituents of the metal and glass are not unlike those found in naturally occurring materials in the marine environment. Of these, only iron and tin are

significantly enhanced in the waste stream relative to the concentrations found in typical marine sediments.

- The material, discharged as a whole, sinks rapidly through the water column. This result indicates that the waste will have minimal impact in the water column and that its dominant fate and effects will occur on the sea floor. Based on the measured sink rates and estimates of shore-ward transport in Special Areas, it is unlikely that the material will be a source of coastal litter if the bags are discharged outside the regulatory limits of 12 nmi or even 3 nmi.
- The ultimate fate of the material is deposition, corrosion, and burial on the sea floor. Corrosion of the metal is likely to occur over several years, although the rates can be highly variable. Corrosion is a process that will lead to a change in the aesthetic nature of the waste stream from a component of litter to a component more typical of sedimentary materials. The time scales for burial and redistribution of metal and glass waste on the sea floor can be relatively long, ranging to hundreds of years for complete burial and degradation.
- Seawater leaching of the metal/glass was shown to cause some effects under laboratory conditions. However, the biological effects were shown to occur at concentrations that are estimated to occur within a few centimeters of the bag. Colonization of the metal and glass components in San Diego Bay over a year showed a highly diverse array of organisms, suggesting that many organisms are not negatively affected by the material.
- The annual input of the metal/glass waste stream from U.S. Navy ships operating in Special Areas constitutes a tiny fraction of basin-wide inputs. It is estimated that it would take hundreds to billions of years of U.S. Navy discharges to match a single year discharge from other basin sources such as rivers or industrial discharges. The amount of material discharged annually by U.S. Navy ships would cover only a tiny fraction (billionths) of the sea floor.
- From a basin-wide perspective, there is at least a billion times more oxygen available in Special Areas than is needed to completely oxidize the annual discharge of metal components of the waste stream, implying that it is improbable that the discharges will have any impact on the oxygen budget of any of the seas.

## **5.0 REGULATORY FRAMEWORK**

MARPOL Annex V restricts solid waste discharge at sea within specific distances from shore and within Special Areas. Warships are exempt from the restrictions, but are expected to comply to the extent “reasonable and practicable”. The basic requirements of MARPOL Annex V are:

- Disposal of all plastics into the sea is prohibited; disposal of dunnage, lining, and packing material that will float is prohibited within 25 nmi of the nearest land;
- Disposal of food waste and other garbage is prohibited within 12 nmi of the nearest land, unless the waste is comminuted and able to pass through a 12 mm screen, in which case disposal is permitted beyond 3 nmi from the nearest land;
- Disposal of all garbage (except food waste beyond 12 nmi) is prohibited in designated Special Areas that are in-effect.

The Act to Prevent Pollution from Ships (APPS), as amended by the Marine Plastic Pollution Research and Control Act of 1987, the National Defense Authorization Act for FY 1994 (DAA-94), and the National Defense Authorization Act for FY 1997 (DAA-97), implements MARPOL Annex V for the U.S.

### **5.1 OPNAVINST 5090.1B GUIDE FOR SUBMARINES**

The Navy currently follows the guidelines for submarine solid waste discharges prescribed by OPNAVINST 5090.1B. These guidelines are summarized below:

- Submarines shall limit plastics discharges to the minimum amount practicable. Buoyant garbage discharges from submarines are prohibited;
- Submarines may discharge non-plastic, compacted, sinkable garbage between 12 nmi and 25 nmi if the water depth is greater than 1000 fathoms, and beyond 25 nmi in any water depth;
- Currently under APPS, the Secretary of Defense is required to report annually in the Federal Register on the amount and nature of discharges in Special Areas in-effect in which the discharge did not meet Annex V limitations;
- Submarines must comply with both the MARPOL Annex V plastic discharge prohibition and the Special Area requirements by 1 January 2009.

### **5.2 SPECIAL AREA RATIONALE**

To be classified as a Special Area, all bordering countries must determine whether that region mandates special interest and why. Mandatory methods for the prevention of sea pollution by garbage are required in Special Areas due to sensitive oceanographic and ecological conditions, and to the particular character of the vessel traffic within the region. MARPOL Special Areas negotiated through the International Maritime Organization (IMO) include the Baltic Sea, the North Sea, the Mediterranean Sea, the Wider Caribbean Region (including the Gulf of Mexico and the Caribbean Sea), the Antarctic Area, the Black Sea, the Red Sea, and the "Gulfs" Area that includes the Persian Gulf and the Gulf of Oman. Of these regions, full implementation of the discharge restrictions are currently “in-effect” for only the Antarctic Area, North Sea, and Baltic Sea.

## 6.0 OPERATIONAL PROFILES

One of the most comprehensive studies on submarine operations and trash disposal practices was conducted and published by NNS under contract to NAVSEA in November 1994. This study includes the data collection from existing platforms which provides sufficient waste generation figures with which to discuss current operational profiles. In addition, COMSUBLANT and COMSUBPAC, responding to requests from NAVSEA, have provided information regarding patrol days for the last three years in Special Areas. Other information, on patrol days from the Center for Naval Analyses and TDU use on operating submarines from submarine platforms, have provided supplemental data for this environmental analysis.

Submarines are highly specialized vessels with very demanding requirements for operation. They comprise only about 25% of the U.S. Navy fleet and carry a significantly smaller complement than the majority of surface vessels, averaging approximately 130 crew members. Submarines have unique specifications for space, weight, shock, safety, acoustic, and atmospheric-control requirements. They operate for long periods of time, up to months, without surfacing or replenishing supplies in order to accomplish their missions. Personnel aboard submarines live and work in extremely tight spaces, and storage space is very limited. These special conditions lead to a limitation in the options available to submarines for handling solid waste.

### 6.1 WASTE GENERATION

Waste generation aboard submarines is typically lower than that of surface ships, ostensibly as a result of constraints on stowage. Solid waste generation rates from the NNS study in 1994 indicate a total paper, cardboard, metal, and glass generation rate of  $0.21\text{--}0.49\text{ kg}\cdot\text{person}^{-1}\cdot\text{d}^{-1}$  (table 6-1). This is in comparison to a surface ship generation rate of the same materials of  $0.75\text{ kg}\cdot\text{person}^{-1}\cdot\text{d}^{-1}$  (Schultz and Upton, 1988). This reduced rate for submarines seems quite reasonable in light of the efforts made to minimize packaging materials stored aboard because of restricted storage space. Even though the total generation rates are different, the percentage (by weight) of the materials generated, roughly 60% paper and cardboard, 30% metal, and 10% glass, is reasonably similar (Schultz and Upton, 1988).

The differences in solid waste generation rates between the USS *Cincinnati* and the USS *Kamehameha* (shown in table 6-1) were described in the NNS study (1994) as due to differences in crew habits, menus, variations in at-sea time, and differences in waste reduction efforts. It was noted that some boats, including the USS *Kamehameha*, have implemented special methods to significantly reduce their waste, which may also explain the difference with the USS *Cincinnati*, which had not implemented these methods. Currently, these methods are being evaluated and implemented on other fleet assets. For this study, the higher generation rates of paper, cardboard, metal, and glass measured aboard the USS *Cincinnati* ( $0.49\text{ kg}\cdot\text{person}^{-1}\cdot\text{d}^{-1}$ ) will be used to provide conservative estimates of mass loading.

Table 6-1. Summary of submarine solid waste generation rate data (NNS, 1994).

Trash Type	Generation Rate (kg·person <sup>-1</sup> ·d <sup>-1</sup> )	Total of PCMG (%)	Generation Rate (kg·person <sup>-1</sup> ·d <sup>-1</sup> )	Total of PCMG (%)
	Submarine USS <i>Cincinnati</i>		Submarine USS <i>Kamehameha</i>	
Cardboard	0.21		0.05	
Paper (FC)	0.06		0.06	
Paper (NFC)	0.03		0.01	
Textiles	0.03		0	
Plastic (FC)	0.06		0.04	
Plastic (NFC)	0.07		0	
Metal (FC)	0.14		0.10	
Glass (FC)	0.05		0	
Total	0.65		0.25	
PCMG Total	0.49		0.21	
Paper/Cardboard		61		53
Metal		28		47
Glass		10		0

FC = Food contaminated trash

NFC = Non-food contaminated trash

PCMG = Totals for paper, cardboard, metal and glass only

Data on the generation rates of oily paper towels aboard submarines come from a report prepared for NAVSEA PMS393 by Newport News Shipbuilding (NNS, 1996). In this report 14 SSN 688 Class submarines were interviewed with regard to their use of oily paper towels, primarily generated from clean up of lubricating oil. The rough order of magnitude volume generation rate of oily paper towels varied from 3.7 to 18.9 L·d<sup>-1</sup>, and averaged 9.4 L·d<sup>-1</sup>. With a TDU can internal capacity of 25 L, the average generation rate would fill roughly 28% (by volume) of one TDU can each day, using the NNS, 1996 assumption that the paper towels will compact to about 75% of their original volume. A rough mass-to-volume measurement of cloth materials suggest that the bulk density of paper towels would be very roughly 0.24 g·cm<sup>-3</sup>. Using this density value, the 9.4 L·d<sup>-1</sup> rate and a 75% compaction ratio would translate into roughly 3 kg of oily paper towels per day. This generation rate will be used for the assessment of oily paper towels that will potentially be added to the paper, cardboard, metal, and glass waste stream.

Given the above generation rates, and a typical complement of 130 persons aboard submarines, the total paper, cardboard, metal and glass produced daily is approximately 64 kg. The additional amount of oily paper towels would bring the daily solid waste total to about 67 kg. To be in compliance with TDU system manuals (S9SSN-W4-SSM-JDO), discharged TDU cans should weigh between 25.6 and 29.0 kg. According to waste generation rates, a minimum of about three TDU cans would be discharged each day, considering that a portion of the total weight is related to the TDU can itself and the steel weights used for ballast. To compute the mass fraction of materials making up a full discharged can, it is assumed that the total can weight is 28 kg that there are two weights added per container (NNS, 1994), and that the contents of each can are in proportion to the amounts generated daily. Thus, the contents of each can are fixed, would total about 21 kg, and be made up roughly of 12 kg paper/cardboard, 6 kg metal, 2 kg glass, and 1 kg oily paper towels. Results of this computation are shown in table 6-2.

Table 6-2. Amount and percentage (by weight) of materials making up a typical TDU container and its contents.

Material type	Weight (kg)	Mass Fraction of Total Package
TDU Container	2	7.1%
Weights (2 per can)	5	17.9%
Paper/Cardboard	12	42.9%
Metal	6	21.4%
Glass	2	7.1%
Oily Paper towels	1	3.6%
Total	28	100%
Contents Only	21	75.0%

Mass loading estimates in Special Areas will be based on the daily generation rates of the waste components, including the can and ballasting materials as described above. Although the solid waste generation rates support a minimum discharge rate of three cans per submarine per day, crew interviews suggest that the number of TDU cans discharged per day averages about 7 (NNS, 1994). Given the high likelihood that more TDU cans may be used than the minimally required amount due to variations in compacted volume of the waste, estimates of the basin-wide sea floor coverage by TDU containers will be made on the basis of a discharge rate of  $7 \text{ d}^{-1}$ . While this estimate will be conservative from the viewpoint of sea floor coverage, the difference in the amount and mass fraction of materials in each container versus the typical container described in table 6-2 will not be taken into account (e.g., additional container and ballasting material).

Because submarines do not generally travel in groups, local scale impacts are considered only from discharges by a single platform. However, an analysis of a basin-wide scale will be included for comparison to other anthropogenic, natural, and U.S. Navy surface ship inputs.

## 6.2 SHIP OPERATIONS

Because submarine operation data are sensitive, data obtained from COMSUBPAC and COMSUBLANT are summarized here only in generic terms. For the 1993 to 1995 period, the total number of patrol days in Special Areas averaged between 40 and 925 per year. The number of submarine mandays in Special Areas, based on the range in patrol days and a crew complement of 130, ranges from 5200 to 120,250. Based on a similar analysis performed on historical surface ship data (Chadwick et al., 1996), mandays for surface ships range from 0 (there is no surface traffic in the Antarctic Region) to 3,400,000. Based on these data, it is clear that submarine traffic is significantly lower, by as much as 100 times lower, than surface ship traffic in Special Areas.

There are approximately 11,000 total submarine operating days per year (Commander Perry, personal communication). Of these, 1800 or so operating days are conducted in Special Areas. Although the number of operational days in open oceans is substantially greater than those occurring in Special Areas so is the relative surface area of the world's oceans to that of Special Areas ( $3.61 \cdot 10^8 \text{ km}^2$  cf.  $4.3 \cdot 10^7 \text{ km}^2$ ). The density of submarine operations in Special Areas (patrol days/surface area) is thus greater than that of the open ocean.

## 7.0 WASTE STREAM CHARACTERIZATION

The submarine TDU waste stream consists of paper, cardboard, metal cans made of aluminum and tin-coated steel, glass, oily paper towels, and metal weights, all compressed inside a perforated metal container. The discrete nature of the packaging of the TDU waste stream makes it somewhat comparable to that of the burlap bags containing shredded metal and glass discharged from surface ships. Differences between these discrete discharges are that the TDU containers will contain compressed paper and cardboard, compressed rather than shredded metal and glass, oily paper towels and, of course, the container and weighting materials themselves. Characterization of pulped paper and cardboard and shredded metal and glass was performed previously as part of the surface ship waste discharge assessment (Chadwick et al., 1996). Because much of this work is applicable to the components of the TDU waste stream, the following waste stream characterization focuses on the container, weighting materials, and oily paper towels. While results from the previous characterization work will be used where applicable, consideration will be given to the differences in material type or form (e.g., pulped vs. compressed) where they exist.

Originally, 11 TDU containers were acquired for physical, chemical, and toxicological characterization. Two of the eleven (TDU10 and TDU11) were new, empty containers (see figure 7-1) obtained from the Naval Surface Warfare Center/Carderock Division (CD/NSWC). These two were used for weight and size measurements as well as for chemical composition analysis. Two others (TDU4 and TDU5), obtained from the USS *La Jolla* berthed at the Submarine Base San Diego, were filled with about 8 kg each of compacted paper and cardboard only. These, along with two metal ballasting weights obtained from the USS *La Jolla* were used for toxicity testing. The remaining seven containers were obtained from trash dumpsters located near the piers where the USS *La Jolla* and the USS *Salt Lake City* were docked at the Submarine Base San Diego. One of the seven containers which looked distinctly different than the others was constructed of galvanized material. None of the seven containers were filled the way they would be for disposal at sea, and none of the them had metal weights added. The cans contained a mixture of materials including paper, cardboard, tin cans, wet bags, food wastes, plastics, and textiles. The presence of plastic, food, wet bags, and textiles, as well as the lack of weights in the cans, was a result of the intention to dispose them ashore. Some of these seven cans were used for sinking tests and long-term integrity tests. TDU3 was also used for chemical composition analysis.

At a later date, another six TDU cans were obtained for chemical and toxicological analysis from the USS *La Jolla*. Three of the cans contained compressed paper, cardboard, metal, glass, and ballasting weights while the other three also contained oily paper towels. The contents were present in proportions typical of submarine generation rates, roughly 13.6-kg paper/cardboard, 4.5-kg metal, 2.3-kg glass, 1-kg oily paper towels, and 5-kg ballasting weights.

### 7.1 PHYSICAL ANALYSES

**Weight and Size Analyses.** Containers and steel weights were weighed using a spring scale. Empty containers weighed 2.0 kg while filled containers ranged from 9.6 kg to 15.9 kg (table 7-1 below). Two steel weights were 2.3 and 3.2 kg, each. The containers measured 60 cm long by 23 cm in diameter, giving an external surface area of 5165 cm<sup>2</sup> and an internal volume of 25 L.



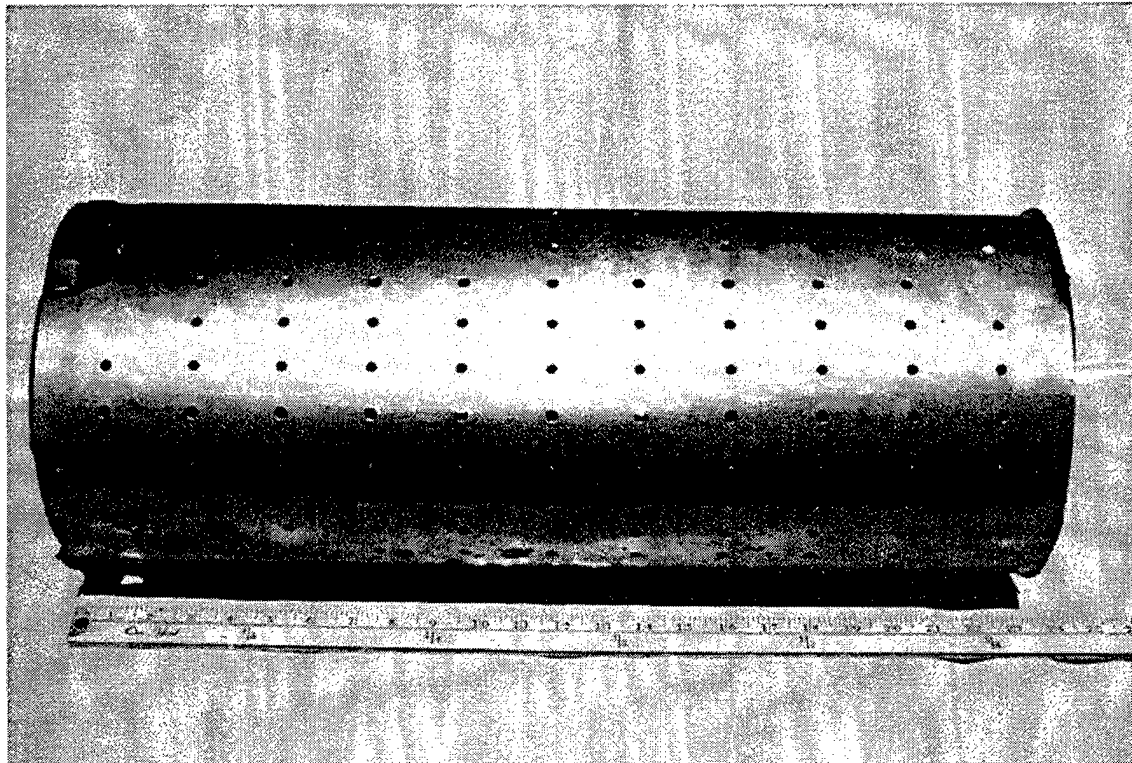


Figure 7-1. Unfilled TDU container obtained from CD/NSWC.

**Contents Identification.** The specific contents of cans obtained for this study were not identified, as they were considered to be either non-representative of components normally present for at-sea discharge, or were generated for specific purposes. Their general makeup however, is shown in table 7-1. In the absence of new measurements, the USS *Cincinnati* generation rate data (NNS, 1994) is used to estimate the proportions of the various material types present in a typical container (table 6-2).

**Settling Velocity.** Settling velocity tests were conducted on two cans (TDU2 and TDU7) by dropping them off the RV *Ecos* into the waters of San Diego Bay. The two cylinders were placed just below the water surface, allowed to purge any trapped air, then allowed to freely fall about 13 meters to the bottom. The drop speed was measured using a KPSI pressure transducer attached to the side of the cylinder. Depth as a function of time was logged onto a data acquisition computer system at a rate of 3 Hz.

Each can's settling velocity was measured under four weight conditions. The first condition was using the can with its original weight condition. Under the second and third condition, weights were added to one end of each can. To partially compensate for the original weight difference of the two cans, more weight was added to TDU7 than to TDU2. Under the third condition, the cans weighed 27.6 and 25.4 kg, which is in the range instructed by the TDU system manual (S9SSN-W4-SSM-JDO) for discharge. In the last configuration, the weights used for condition 3 above were split and added to both ends of the cans to balance the load. Replicate measurements were made under each of the four weight conditions.

Table 7-1. Weight and contents of TDU containers obtained for this study.

TDU Container	Weight (kg)	Contents
1	10.9	Mixed Materials
2	18.6	Mixed Materials
3	14.1	Mixed Materials
4	9.6	Paper/Cardboard Only
5	10.0	Paper/Cardboard Only
6	15.9	Mixed Materials
7	12.7	Mixed Materials
8	14.1	Mixed Materials
9	15.9	Mixed Materials
10	2.0	Empty
11	2.0	Empty
12	28.0	PCMG
13	28.0	PCMG
14	28.0	PCMG
15	28.0	PCMG and oily paper towels
16	28.0	PCMG and oily paper towels
17	28.0	PCMG and oily paper towels

\* PCMG = Paper, cardboard, metal, and glass.

Results of the four sets of tests are shown below in table 7-2. Settling velocities ranged from 58.4 to 137.6 m·min<sup>-1</sup>. These rates are all significantly higher than the average fall velocity of 32 m·min<sup>-1</sup> measured for shredder bags discharged from surface ships. Maximum rates were observed when the cans were fully loaded and the weights were added at one end. The maximum settling rate averaged for the two cans was 133 m·min<sup>-1</sup>. The velocities increased linearly with increasing weight for each can, although each can had its own settling characteristic (figure 7-2). Splitting the weights reduced the settling rate by 40%. The cans reached terminal velocity within the first few seconds of sinking (figure 7-3) and, thus, it is expected that the impacts to the bottom observed in these tests would not be altered by an increase in water depth. An observation made during these tests was that the cans weighted at one end sank “end-on” while the cans weighted at both ends sank “side-on”.

The results of the settling tests indicate that the cans will reach the sea floor very rapidly in all Special Areas. Settling times would range from 16 seconds in the Persian Gulf to just over 11 minutes in the Mediterranean, given their average bottom depths of 36 and 1500 m, respectively, and average settling rates of fully weighted (one-end) cans. The implication of these results is that exposure in the water column should be insignificant from either a toxicity or beach litter viewpoint. This is true even using the reduced settling rates caused by changing the weight distribution of the cans. In this latter case, settling times would be 23 seconds in the Persian Gulf and 16 minutes in the Mediterranean. There is no reason to believe that these results would differ by varying the specific makeup of the container contents.

**Container Integrity.** The settling tests described above were performed over a reasonably hard sandy bottom. Each can was dropped at least eight times without any observed effect on the physical integrity of the can. Because the cans were at terminal velocity when impacting the bottom, the results indicate that the cans should remain intact after hitting the bottom under most sea floor conditions. A possible exception to this might occur over a rocky sea floor.

Table 7-2. Settling velocity of TDU containers under four weight conditions. The last two weight conditions are in the range directed by S9SSN-W4-SSM-JDO for discharge.

Weight Condition	Weight (kg)		Settling Velocity m·min <sup>-1</sup>		
	TDU2	TDU7	TDU2	TDU7	AVG
Original Weight	18.6	12.7	65.7	58.4	62.0
with 4.5 or 8.2 kg*	23.2	20.9	96.1	104.7	100.4
with 9.0 or 12.7 kg*	27.7	25.4	128.5	137.6	133.0
with 9.0 or 12.7 kg* "split weights"	27.7	25.4	89.1	95.7	92.4

\* Different weights were added to partially compensate for different starting weight of the cans.

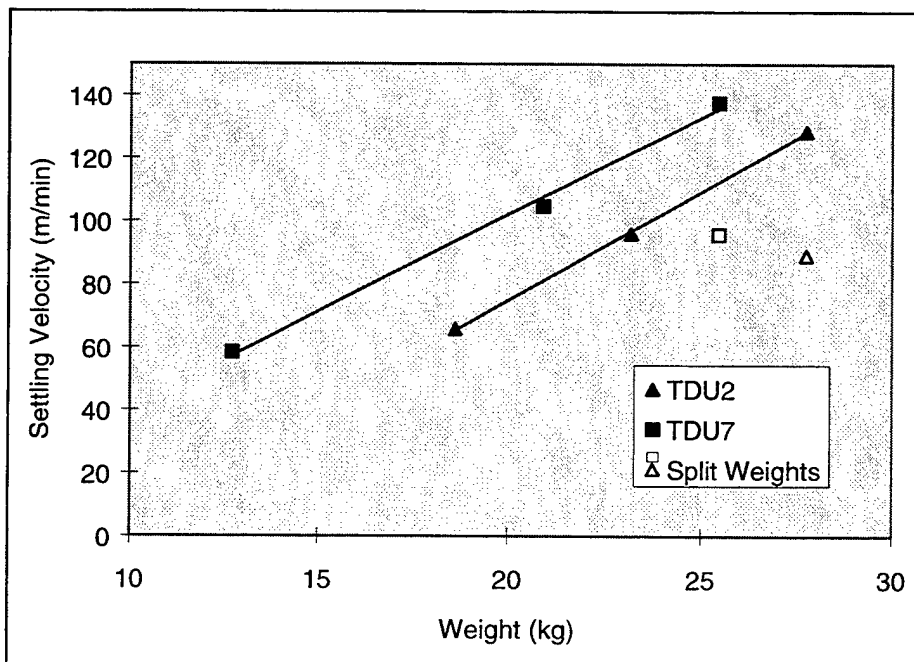


Figure 7-2. Settling velocity of containers TDU2 and TDU7 as a function of total weight. The maximum weight tested for each container fell within the range instructed by the TDU system manual (S9SSN-W4-SSM-JDO) for discharge. The open symbols represent the results of splitting the weights added to both ends of the containers.

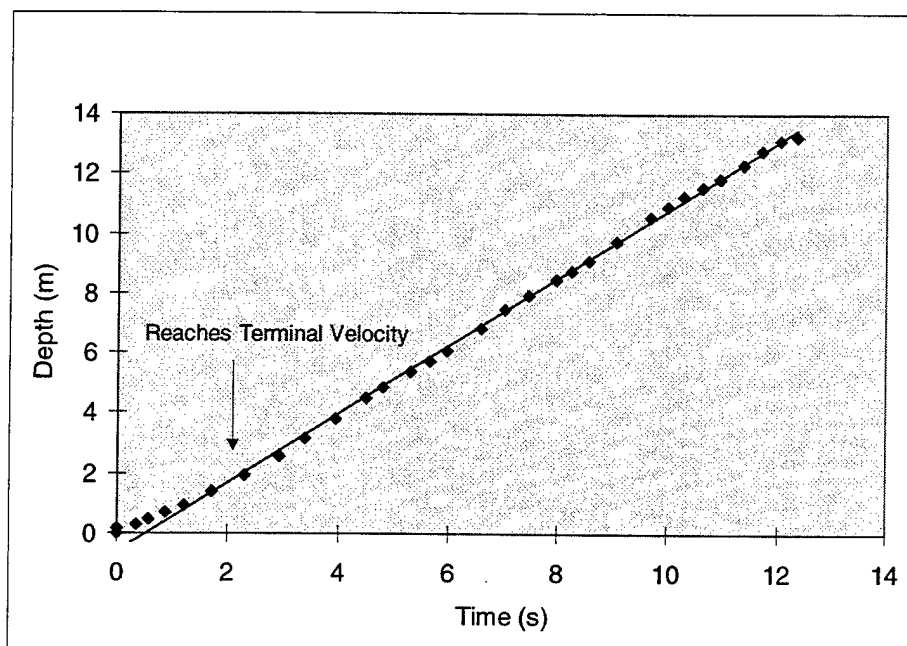


Figure 7-3. Depth as a function of time for one TDU settling velocity test. Constant velocity was reached within about 3 seconds, indicating that the container had reached terminal velocity at that point.

## 7.2 CHEMICAL ANALYSES

Chemical analyses performed as part of this study include a priority pollutant scan on seawater leachates of TDU cans and their contents and an elemental analysis of the cans and ballasting weights. Data on the chemical constituents and degradation or corrosion rates of paper, cardboard, metal, and glass components are derived primarily from the waste stream characterization for surface ships (Chadwick et al., 1996) and are supplemented with new data relevant to variations in the form of the waste (e.g., compressed vs. pulped).

Two types of chemical analyses were performed on TDU containers. A 126 priority pollutant chemical scan (40 CFR 136) was made on seawater leachates of two TDU containers holding only compressed paper and cardboard and a metal weight (TDU4 and TDU5); on two containers holding compressed paper, cardboard, metal, glass, and two ballasting weights (TDU12 and TDU13); and on two containers holding oily paper towels in addition to the paper, cardboard, metal, glass, and ballasting weights (TDU15 and TDU16). All of these analyses were performed by MEC Analytical Systems, Inc. in conjunction with a toxicological assessment of the leachate. Their report is included in Appendix A. Two containers, TDU3 and TDU10, and one ballasting weight were also analyzed for their elemental composition to estimate their likely corrosion rates in seawater. This analysis was performed by the Materials Science Branch of NCCOSC RDT&E Division, Code D662, and is described below in the corrosion section, with a full report in Appendix C.

**Seawater Elutriate Preparation.** Seawater leachates of TDU4, TDU5, TDU12, TDU13, TDU15, and TDU16, each with their contents, were prepared for chemical and bioassay analyses. The solutions were produced using a method derived from the Army Corps of Engineers "Green Book" (U.S. EPA, 1991) developed for dredge spoil analyses. The cans with their associated material were soaked for 1.5 hours in "clean" filtered seawater obtained from the

Scripps Institute of Oceanography seawater facility. All cans except TDU5 were soaked in an amount of seawater equivalent to four times its weight while TDU5 was soaked in an amount of seawater equivalent to 20 times its weight. The "Green Book" method actually dictates that the leachate be produced from soaking material at a 4:1 ratio by volume rather than by weight. Because the internal air space of the containers was not known, it was felt that a weight analysis would be more appropriate. The effect of performing the analysis on a weight basis is about the same or even more conservative, i.e., instead of soaking a 25 L can in 100 L of water, the containers weighing about 12 to 28 kg were soaked in 52 to 112 kg of seawater. The purpose of preparing a leachate at the 20:1 concentration (TDU5) was to see if it was possible to bracket the toxicity results with a no-effects level.

In addition to these standardized leachate preparations, leachates of cans TDU14 and TDU17 were made by placing them on the bottom of San Diego Bay and extracting seawater out of their interiors and at 50 cm from their surface after 24 hours. These non-standard, *in situ* leachates were generated to look at the relationship between some laboratory toxicity testing results and those measured under real-world conditions.

**Full Waste Stream Priority Pollutant Scan.** The 126 priority pollutant scan of seawater leachates obtained from the complete TDU waste stream, with and without oily paper towels, indicated the following analytes present at levels above method detection limits: zinc, copper, total phenolics, and two phthalate esters; dimethyl- and Bis(2-ethylhexyl) phthalate. The analytical results are summarized in table 7-3 along with water quality criteria (WQC) set by the Environmental Protection Agency (EPA) in *Quality Criteria for Water 1986* (U.S. EPA, 1987). The complete results can be found in Appendix A. Leachates from all four containers and their contents showed zinc at a consistent value of about 22 ppb. One leachate (TDU15) also contained copper at 191 ppb and dimethyl phthalate at 11 ppb. One leachate (TDU13) contained total phenolics at 50 ppb, which was primarily made up of phenol (34 ppb). One leachate (TDU12) contained Bis(2-ethylhexyl) phthalate at 15 ppb. The remaining analytes measured in this analysis, including metals, volatile organics, semi-volatile organics, organochlorine pesticides, and polychlorinated biphenyls were all reported at non-detectable levels.

Table 7-3. Results of a 126 priority pollutant scan of seawater leachates made from TDU cans containing paper, cardboard, metal, glass (TDU12 and TDU13) and oily paper towels (TDU15 and TDU16). All concentrations are reported in parts-per-billion (ppb). An "nd" indicates not detected. Included in the table are water quality criteria (WQC) set by the EPA (U.S. EPA, 1987).

Analyte	TDU12	TDU13	TDU15	TDU16	Marine Acute WQC	Marine Chronic WQC
Zinc	23	21	23	21	98	86
Copper	nd	nd	191	nd	2.9	2.9
Total Phenolics	nd	50	nd	nd	none	none
Phenol	nd	34	nd	nd	5800*	none
Dimethyl Phthalate	nd	nd	11	nd	2944*	3.4*
Bis(2-ethylhexyl) phthalate	15	nd	nd	nd	2944*	3.4*

\* Lowest observable effect level as there are insufficient data available to develop criteria.

Of the 126 priority pollutant analytes observed at detectable levels, only zinc was found in all samples. This includes the analyses performed on TDU4 containing only paper/cardboard and a ballasting weight. This suggests that the zinc is fluxing off of these materials rather than from the glass, metal, or oily paper towel portion of the contents. The likely source of the zinc is the paper and cardboard material, as zinc was found in the shredded paper and cardboard waste stream at  $5.6 \text{ mg}\cdot\text{kg}^{-1}$  (Chadwick et al., 1996), and there is no evidence for zinc in either the containers or ballasting weight (see elemental analysis below) or in the metal or glass contents (Chadwick et al., 1996). The 22-ppb concentration measured in the leachate is less than the marine acute (95 ppb) or marine chronic (86 ppb) WQC set by the EPA.

The presence of copper (191) in only a single leachate is considered an anomalous result for TDU cans in general. Submarines and surface ships generate identical solid waste materials. The only difference between the two is the manner in which the materials are processed for discharge. In the surface ship solid waste stream characterization (Chadwick et al., 1996), aluminum cans were found to contain copper at 0.2% levels and steel cans contained copper at 0.1%. In addition, each TDU container is supplied with two ballasting weights that contain 0.5% copper in the alloyed form. However, copper was not observed in the leachates of any of the other cans containing copper alloyed material. This suggests that the source of the high copper leachate was, in fact, not from the copper alloyed materials typically discharged in TDU cans but from an irregular item of waste containing solid copper salts. This was, most probably, from a piece of waste copper piping or pipe fitting containing corrosion products which readily leached copper ions. The Standard Submarine Organization and Regulations Manuals (SSN) (COMSUBLANT/COMSUBPACINST 5400.38 and 5400.39, 1993), specifically prohibits the disposal through the trash disposal unit of "large or odd-shaped pieces of metal". Therefore, the TDU discharges containing high levels of copper are considered highly unlikely.

The source of phenols and phthalates in the leachate is not known. Phenols can result from the degradation of organic matter and phthalates are used in the production of a wide range of products including packaging materials and textiles. While there are no specific EPA WQC for these compounds, the lowest observable effects concentrations of 5800 ppb for phenol and 2944 ppb (acute) and 3.4 ppb (chronic) for phthalate esters are shown in table 7-3 for comparison. In the case of phenols, the amount measured in the leachates is over 100 times lower than the lowest observable effects concentration. Both phthalates (11 and 15 ppb) are well below the acute effects concentration indicated, but are above the chronic effects concentration.

**Paper/Cardboard Chemistry.** The following is a summary of the waste stream chemical characterization for the paper and cardboard found in Chadwick et al., 1996. Chemical analyses of the paper and cardboard waste stream were performed on both seawater slurries and on bulk material derived from the pulping process. As such, the material tested is slightly modified from the form expected to be found within the TDU containers. The principal difference is that the material expected in the cans will be compressed rather than ground up into small particles. This will have no effect on the chemistry of the material although the reduced surface area to volume of the compressed paper may have an impact on the ability of microorganisms to interact with the material. This could impact the material's eventual degradation rate and potentially lower its Biochemical Oxygen Demand (BOD), which is discussed below.

Paper and cardboard is primarily composed of organic cellulosic material. Measurements indicate that between 92% and 98% of the material is cellulose, with the rest primarily fillers that

are composed of inorganic oxides of calcium, titanium, aluminum, and silicon (Glad, 1996). Consistent with the chemical composition of cellulose ( $C_6H_{10}O_5$ )<sub>n</sub>, the pulped material is mainly composed of organic carbon with very little nitrogen or phosphorous. The ratio of C:N:P (by weight) in the solid phase of the pulped material is roughly 2000:1.3:0.15 compared to average values for naturally occurring marine organic matter that has C:N:P ratios of roughly 41:7.2:1 (Redfield, 1934), for treated municipal sewage with C:N:P of 17:7.5:1 (Wastewater Chemistry Laboratory, 1994), and marine sediments with C:N of 56:6 (Sverdrup et al., 1942). This result has two primary implications. First, it implies that the nutrient loading from the pulper effluent will be low relative to other sources of particulate organic material in the ocean. This suggests that productivity should not be significantly enhanced by the waste stream and thus eutrophication should not be a major impact. The second implication is that because of its low nutrient content, the material is not the best source of carbon for marine bacteria.

The slow degradation of pulped paper is reflected in the five-day Biochemical Oxygen Demand (BOD<sub>5</sub>) and Chemical Oxygen Demand (COD) values measured by Chadwick et al., 1996. The BOD<sub>5</sub> value was about 0.07 g·g<sup>-1</sup>, consistent with published values for cellulose of 0.08 g·g<sup>-1</sup> BOD<sub>5</sub> (Furness et al., 1990). However, a COD level of 0.14 g·g<sup>-1</sup> is considerably lower than the theoretical total oxygen demand value of 1.18 g·g<sup>-1</sup> required for complete oxidation of cellulose. This may be due to incomplete oxidation in the COD test as suggested by Pitter and Chudoba (1990). The BOD<sub>5</sub> and COD levels are also relatively lower than those found in sewage treatment plant influents (Wastewater Chemistry Laboratory, 1994) or in discharge effluent not subjected to primary treatment (Pyewipe, 1992-1994). The amount of organic carbon and high surface area of the particles generated in the pulping process is sufficient to generate these levels. It should be noted that although cellulose has the same basic molecular makeup as starch, the BOD<sub>5</sub> of starch is 7 times greater at 0.62 g·g<sup>-1</sup> (Pitter et al., 1990). This suggests a substantially lower degradability of the cellulose relative to starch as a result of structural differences.

A priority pollutant analysis of paper/cardboard performed by Chadwick et al., 1996 showed no pollutants at levels which would be expected to produce impacts. All 126 compounds were below the detection limit of the analyses performed except for zinc at 5.6 mg·kg<sup>-1</sup>, acetone at 1.8 mg·kg<sup>-1</sup>, and a few aliphatic hydrocarbons between C<sub>16</sub> and C<sub>20</sub> at 6 mg·kg<sup>-1</sup> (all on a dry weight basis). The presence of zinc at 5.6 mg·kg<sup>-1</sup> dry weight is a factor of 25 below the Effects Range Low (ERL) threshold of 150 mg·kg<sup>-1</sup> for zinc in sediments (Long et al., 1995), a guideline for concentrations representing minimal toxicity effects. It is also well below the 960 mg·kg<sup>-1</sup> screening level guideline for sediments, using Sediment Management Standards (1991), one of the only sources for sediment quality guidelines. The presence of aliphatic hydrocarbons at the low levels observed are indicative of background values that would naturally be present in the marine environment, and as such, do not constitute a contaminant. There are no water or sediment quality criteria for acetone. The only hazard criterion available to compare it with is the Material Safety Data Sheet value for a rat oral lethal dose toxicity of 9750 mg·kg<sup>-1</sup>.

**Paper/Cardboard Degradation.** The long-term fate of paper/cardboard in the ocean will partially be controlled by the rate of microbial degradation. Relatively little is currently known about the biological fate of cellulosic material in the open ocean or the cellulolytic abilities of natural oceanic bacterial assemblages, primarily because cellulose is not naturally abundant in such environments. Therefore an experimental study was conducted at the University of Georgia to measure microbial degradation rates of pulped and compressed paper and cardboard in the open ocean environment. Factors that may regulate microbial degradation of the pulped paper include background abundance of cellulolytic organisms, particle size and structure, temperature,

pressure, and redox conditions experienced by the attached bacterial community. Initial laboratory tests of the solid-phase pulper material indicated first-order degradation rates of about  $0.5\% \cdot d^{-1}$  as an upper limit to degradation in seawater when temperatures were optimal ( $28^{\circ}C$ ) and excess inorganic nutrients were available (Chadwick et al., 1996). Previous studies have shown that cellulose decomposition rates increase by threefold to fourfold (Q10) when incubation temperatures are increased from  $10^{\circ}$  to  $20^{\circ}C$  (Benner et al., 1986). Using the degradation rates from the laboratory and the Q10 value of Benner et al., 1986, degradation rate estimates of pulped paper and cardboard in Special Areas are expected to vary from about  $0.01\% \cdot d^{-1}$  in the cold bottom waters of the Caribbean to  $0.6\% \cdot d^{-1}$  in the warm surface waters of the Mediterranean.

As mentioned previously, cellulose degradation studies conducted by the University of Georgia for the surface ship waste discharge program were extended to include non-pulped paper and cardboard tests. The experiments were designed to measure rates of degradation of pieces of cardboard and white paper (unpulped material) in seawater at low temperature. Corrugated cardboard and office photocopy paper (with ink printing on the paper) were cut into  $3\text{ cm} \times 1\text{ cm}$  pieces and placed individually into 120-ml glass BOD bottles filled with an artificial seawater amended with inorganic nutrients ( $5\text{ }\mu\text{M N}$  and  $1\text{ }\mu\text{M P}$ ) and inoculated with marine bacterioplankton. Bottles were placed in an incubator at  $4^{\circ}C$ . At approximately weekly intervals, three bottles of each cellulose type (cardboard or paper) were titrated for dissolved oxygen concentration using an automated precision Winkler method. Three control bottles (no paper or cardboard added) were also titrated at each time point. Cumulative oxygen consumption in the BOD bottles (corrected for consumption in the controls) was used to estimate bacterial mineralization of cellulosic carbon. The cardboard and paper sources were analyzed at the University of Georgia Chemical Analysis Laboratory and were found to contain 43.5% (cardboard) and 37.6% (white paper) carbon by weight.

Rates of degradation at the end of the 3-week experiment indicated that 0.15% of the cardboard was degraded in a 30-day period, while 0.82% of the white paper degraded in 30 days. The kinetics of degradation indicated a gradual increase in the decomposition rate throughout the experiment (i.e., the decomposition constant " $k$ " for cardboard increased from  $1.37 \cdot 10^{-5}$  after 5 days to  $4.85 \cdot 10^{-5}\text{ d}^{-1}$  by Day 21; likewise, the  $k$  for white paper increased from  $6.48 \cdot 10^{-5}$  to  $27 \cdot 10^{-5}\text{ d}^{-1}$ ). This change in  $k$  is inconsistent with what was found for pulped paper, for which decomposition appears to be strictly first order, i.e., constant over time. These results indicate that rates of decomposition increase as the cardboard/paper disintegrates in the seawater, possibly by providing more surface area for bacterial attachment, or because there may be a lag time in bacterial colonization.

The rates of bacterial decomposition measured for cardboard and white paper pieces start out significantly lower than rates for pulped mixed paper under comparable temperature and nutrient conditions. A mixture of pulped paper and cardboard degraded at a rate of 1.3% in 30 days at  $4^{\circ}C$  and high nutrient levels ( $5\text{ }\mu\text{M N}$  and  $1\text{ }\mu\text{M P}$ ). The value of the decomposition constant for pulped mixed paper was  $20.7 \cdot 10^{-5}\text{ d}^{-1}$  and was constant throughout the experiment. This compares to an average degradation rate for a 50:50 mixture of white paper and cardboard pieces of about 0.5% in 30 days with an equivalent  $k$  of  $17 \cdot 10^{-5}\text{ d}^{-1}$ . While the initial degradation rates are lower for the pieces under these conditions, the compressed paper and cardboard in the TDU cans should degrade at roughly the same overall rate as pulped material.



**Container and Weights Elemental Analysis.** Elemental analysis of two containers (TDU3 and 10) and one ballasting weight was performed as a part of a corrosion assessment. Because TDU3 was determined to be constructed of galvanized steel and is not expected to be used in future discharges, the discussion here will focus on the findings for TDU10. The methods employed were Energy Dispersive X-ray Spectroscopy (EDS) in a Scanning Electron Microscope (SEM), Combustion Carbon-Sulfur Analysis, Inductively Coupled Plasma (ICP) Optical Emission Spectroscopy, Optical Metallography, and Spark Emission Spectroscopy. These methods are discussed in more detail in the report found in Appendix C and in Chadwick et al., 1996.

The SEM-EDS analysis, shown in figure 7-4, qualitatively indicates that the main chemical element in the containers was iron (Fe). The analysis was performed on a piece of container that was scraped by a knife and one that was not scraped. The presence of carbon (C) and oxygen (O) only on the container piece that was not scraped suggests that an organic coating, likely an oil-based residue, was present. Because the iron line was clearly seen in this analysis, the coating had to be exceptionally thin, likely sub-micron in thickness, and would be unimportant from a standpoint of corrosion in seawater or as a contaminant.

Carbon-sulfur analysis was used to determine the carbon content of the steel used in the production of the cans and steel weight. Several pieces of the can body, bottom, and top were used for analysis. The results shown below in table 7-4 indicate that the container is made of type 1008 rolled sheet steel. The carbon/sulfur results also indicate that the ballasting weight was made of cast iron.

Quantitative analysis of the container was performed using an ICP optical emission spectrometer while Spark Emission Spectroscopy was used to quantitatively look at the weight because of the presence of insoluble silicon found in cast irons. The results of these analyses, shown in table 7-5, confirm the typical elemental composition of the steel types. Iron made up about 98% of the container and about 96% of the steel weight.

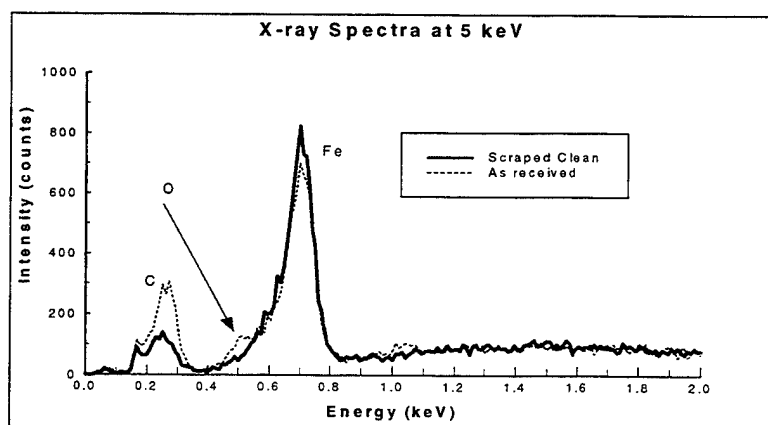


Figure 7-4. SEM-EDS analysis of TDU10. Iron (Fe) is the main elemental constituent. The presence of carbon (C) and oxygen (O) on the unscraped piece suggests an exceptionally thin organic coating residue that is likely oil based.

Optical metallography was employed to determine metal thickness and to characterize the cast iron weight. Metal pieces were mounted, ground, polished, photographed (micrograph), then measured using a calibrated eyepiece reticle. The total thickness of the container pieces

measured from the micrographs was 20 mils (thousandths of an inch). An example of a micrograph of the container body is shown in figure 7-5. The cast iron weight was observed to contain graphite flakes and pearlite that is characteristic of gray cast iron (figure 7-6). These results along with the chemistry data suggest that the weight is SAE grade G2500 gray cast iron. The thickness of the weight, measured with a steel rule, was roughly 750 mils.

Table 7-4. Carbon/Sulfur analysis results of TDU container and steel weight. The results below indicate that the container is made of type 1008 steel and that the ballasting weight is made of cast iron. Concentrations are in weight percent with a balance of Fe.

Sample	Carbon (Wt. %)	Sulfur (Wt. %)
Body #1	0.0732	0.0126
Body #2	0.0716	0.0131
Bottom #1	0.0745	0.0131
Bottom #2	0.0802	0.0128
Top #1	0.0794	0.0127
Top #2	0.0795	0.0129
Top #3	0.0832	0.0129
<b>Average</b>	<b>0.0774</b>	<b>0.0129</b>
Steel Weight	3.28	0.088

Table 7-5. Elemental composition of TDU can and weight based on results of ICP and Spark Emission Spectroscopy. The results indicate that the container is made of type 1008 steel and the ballasting weight is made of cast iron. The container had a balance of 99.7% Fe while the weight had a balance of 96.3% Fe.

Sample	Co	Cr	Cu	Mo	Ni	P	V	Ti	Si	Mn
Concentrations in weight percent, balance is Fe										
Can Body	0.102	0.011	0.003	0.000	0.017	0.002	0.003	0.00	0.00	0.20
Can Bottom	0.108	0.011	0.003	0.000	0.017	0.000	0.002	0.00	0.00	0.20
Can Top	0.066	0.013	0.004	0.000	0.016	0.000	0.000	0.00	0.00	0.20
<b>Average</b>	0.092	0.012	0.003	0.000	0.017	0.001	0.002	0.00	0.00	0.20
Steel Weight	-	0.064	0.480	0.030	0.013	0.080	-	0.019	2.40	0.57

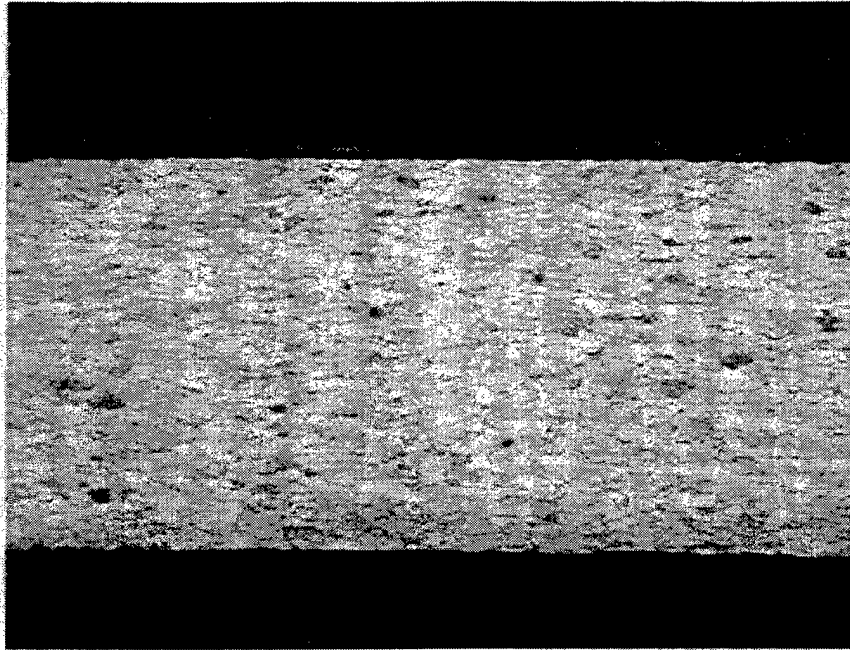


Figure 7-5. Optical micrograph of a TDU container body at 100 x magnification. The wall thickness was measured at 20 mils.



Figure 7-6. Optical micrograph cross-section of cast iron weight at 100 x magnification. The graphite flakes and pearlite are characteristic of gray cast iron.

**Metal and Glass Chemistry.** The following is a summary of the waste stream chemical characterization for the shredded metal and glass found in Chadwick et al., 1996. Although the materials inside the TDU containers will be compressed rather than shredded, the chemical characterization, with the exception of exact percentages, remain the same. The components making up the shredded metal and glass waste stream were shown to be primarily tin-plated steel cans, glass, and organics (food wastes associated with the containers). These were found at 71%, 13%, and 6% by weight, respectively. Minor components included aluminum cans and paper labels each making up about 2% by weight. The burlap bag used to package the metal and glass materials made up the final 8% of the total waste stream.

Based on elemental analysis, the tin-plated steel and aluminum cans were broken down into their major constituents. For steel cans, these were (by weight): iron (98%), tin (1%), and manganese (0.5%). For aluminum cans, these were: aluminum (94%), magnesium (4% max), and manganese (1% max). These materials all form oxides in seawater as part of the corrosion process. The major components of glass bottles include oxides of silicon, sodium, and calcium in typical percentages of 75%, 14%, and 5%, respectively, although the percentages can vary with glass type (Rayotek Scientific, personal communication). The compositional makeup of elements as a percentage of the total waste stream (by weight) are summarized in table 7-6. A comparison of these percentages with those found in average ocean sediments (Chester, 1990) shows that only Fe and Sn were significantly enriched relative to background sedimentary material by factors of 12 and 3500, respectively.

Table 7-6. Elemental makeup of the shredded metal and glass waste stream. Included are comparative values for elemental composition found in average ocean sediments derived from Chester (1990).

Element	Waste Stream	Deep Sea Clays	Waste/Sediments
Fe	70.0%	6.0%	12.0
Si (oxide)	10.0%	55.0%	0.2
Na (oxide)	2.0%	1.5%	1.3
Al	0.9%	10.0%	0.09
Sn	0.7%	0.0002%	3500
Ca (oxide)	0.6%	0.9%	0.7
Mn	0.4%	0.6%	0.7
Mg	0.04%	2.0%	0.02

**Container and Weights Corrosion Analysis.** Reinhart (1976) provides corrosion rate data for type 1010 steel (1008 steel is expected to perform similarly to 1010 steel) and gray cast iron in the marine environment (tables 7-7 and 7-8). The corrosion resistance of the cast iron is somewhat greater than that of steel at higher dissolved oxygen content, but is very similar at lower oxygen levels. At an intermediate corrosion rate of about 2 mpy (mils per year) on each side, a complete container should last about 5 years before it completely corrodes. The cast iron weight, which has a thickness of about 750 mil, would last about 190 years at the same corrosion rate of 2 mpy (both sides). The effect of burial in most cases would not dramatically alter the corrosion rate.

Table 7-7. Corrosion rates for AISI 1010 Steel under varying conditions in seawater (after Reinhart, 1976). Rates are expected to be the same for the TDU container that is a type 1008 steel. Exposed rates are for metal in water only while buried rates refer to metals buried in sediments.

Depth (ft)	O <sub>2</sub> Concentration (mL·L <sup>-1</sup> )	pH	Salinity (psu)	Temperature °C	Exposure time (days)	Rate Exposed (mpy)	Rate Buried (mpy)
5	5.9	8.1	33.51	15	181	9.1	-
5	5.9	8.1	33.51	15	366	8.0	-
5	5.5	8.1	33.31	15	588	8.9	-
2340	0.4	7.5	34.36	5	197	1.6	1.2
2370	0.4	7.5	34.36	5	402	1.1	1.1
5640	1.3	7.6	34.51	2.3	123	2.7	1.9
5640	1.3	7.6	34.51	2.3	751	0.8	0.6
5300	1.2	7.5	34.51	2.6	1064	1.0	0.7
6780	1.6	7.7	34.40	2.2	403	1.9	1.1

Table 7-8. Corrosion rates for Gray Cast Iron under varying conditions in seawater (after Reinhart, 1976). Exposed rates are for metal in water only while buried rates refer to metals buried in sediments.

Depth (ft)	O <sub>2</sub> Concentration (mL·L <sup>-1</sup> )	pH	Salinity (psu)	Temperature °C	Exposure time (days)	Rate Exposed (mpy)	Rate Buried (mpy)
5	5.9	8.1	33.51	15	366	2.6	-
2340	0.4	7.5	34.36	5	197	2.0	0.3
2370	0.4	7.5	34.36	5	402	1.7	2.0
5640	1.3	7.6	34.51	2.3	123	4.2	3.0
5640	1.3	7.6	34.51	2.3	751	1.2	1.0
5300	1.2	7.5	34.51	2.6	1064	0.8	0.5
6780	1.6	7.7	34.40	2.2	403	1.8	1.3

**Shredded Metal Corrosion.** Corrosion rates of the shredded metal waste stream from surface ships were estimated from an elemental analysis of the materials and a literature review of the likely range of corrosion rates expected for those materials in seawater. Although the materials were characterized fairly well, corrosion rates are highly dependent on the receiving environment, particularly on ocean parameters such as oxygen, pH, temperature, pressure, and biofouling. Because the receiving environments of Special Areas span the full range of possible conditions found in the sea, corrosion rates will span a large range. Likely ranges in rates as identified in the corrosion study were 0.6 to 11 mpy for steel cans and 0.1 to 3.9 mpy for aluminum cans. Measured thickness was 0.0067 to 0.00131 inches for steel cans and 0.0043 to 0.133 inches for aluminum cans. Given the range in thickness and corrosion rates, the full range expected for complete corrosion would be 0.6 to 22 years for steel cans and 1 to 130 years for aluminum cans. Using midrange thickness of 0.01 inch for both types of cans, rates of 4 and 1 mpy produce complete corrosion of the steel and aluminum cans in 2.5 and 10 years, respectively. Because of the thinness of the Sn coatings (< 0.00006 inch), even at low measured rates of 0.5 mpy, complete corrosion of Sn will likely occur in about a year.

Compaction of the metals in the TDU cans rather than shredding will reduce the effective surface area available for the corrosion process to occur. However, estimates of corrosion rates and time for full degradation were based on metal can thickness rather than on surface area alone.

Although it is expected that compacting would reduce the overall rate of corrosion relative to that of shredded metal, the differences in time estimates are unlikely to be significant.

Regardless of rates, corrosion of the metal shredder materials is not truly a removal process. It is a mechanism by which the chemical constituents of the cans are redistributed mainly through transition from metal pieces to smaller particles and some dissolution. It also is a mechanism for changing the aesthetic nature of the waste stream from one that is clearly a component of anthropogenic litter to one that may not be recognizable as anything different from typical sedimentary materials. Although variable, the time scale for this to occur will be on the order of years.

**Glass Degradation.** Degradation of glass in the waste stream will occur mainly through the dissolution of its constituent oxides. The susceptibility of glass to fatigue fracture under static loading may also lead to physical degradation as well as an enhanced solubilization of silica within the fractures (Glass Products and Production, 1974), particularly at greater depths. Dissolution of glass, mainly  $\text{SiO}_2$ , will occur because the world's oceans, including Special Areas, are undersaturated with respect to silica. The time constants for these reactions, although poorly known, are exceptionally long, which can be attested to by the fact that there are large silicon-rich deposits distributed throughout much of the world's oceans when, theoretically, there should be none present. In general, Si-rich sediments are found underlying regions of high, primary productivity where the flux of siliceous material to the sea floor is high and where burial rates are high. This suggests that the kinetics of reaction are sufficiently slow enough, relative to burial rates, to allow the material to become incorporated into the sea floor. It is, therefore, likely that any input of glass from the waste stream will be incorporated into the sea floor in a state not much different than its original form.

**Longevity Study.** Although the integrity of a steel TDU container in seawater over time is mainly a function of chemical corrosion, the container and its contents will also undergo changes as a result of recruitment, biological growth, burial by sedimentation, and degradation of the materials. For this reason, a qualitative assessment of three containers on the bottom of San Diego Bay was begun in April 1996 to look at their long-term fate.

Containers TDU1, TDU3, and TDU6 with their contents were placed on the bottom of San Diego Bay on 3 April 1996. The cans were monitored visually by video on 18 April, 3 May, 4 June, and recovered on 14 November 1996. These dates correspond to 15, 30, 62, and 225 days of deployment. After 15 days the cans showed no evidence of biological growth. TDU1 and TDU6 were rusting while the galvanized can (TDU3) remained shiny. After 30 days the cans were coated with a thin layer of sedimentary material. There was evidence of slight biological growth outside the can although it was not clear what type of organisms were present. The galvanized can continued to have a shiny surface with no visual evidence of iron corrosion. After 62 days all the containers had a dusting of sedimentary material. Containers TDU1 and TDU6 showed minor biological growth with some algae or sponge. Additionally, TDU1 had a group of large mussels attached its surface. Because of their size, the mussels appear to have been transplanted from elsewhere rather than recruited as larva. The galvanized can showed no evidence of biological growth and the surface continued to appear shiny.

When the cans were inspected after 225 days, they all had been partially buried and had evidence of light biological growth on their outer surfaces. When recovered, it was observed that all the cans had corroded extensively. The tops and bottoms of the two non-galvanized cans had corroded apart. The zinc coating of the galvanized can had corroded away, and the iron surface was oxidized similarly to that of the other two cans. Small invertebrates such as crabs, octopus, and amphipods were observed crawling out of the can when they were placed on the dock. There was also a strong hydrogen sulfide smell present, and the material inside the cans had blackened.

The results of this long-term deployment of TDU containers differs slightly from those seen for burlap bags containing shredded metal and glass wastes that were monitored for about a year as part of the surface ship work (Chadwick et al., 1996). Both bags and cans were being buried by natural sedimentation. However, while the bags collected sediment all over their surface, the cans seemed to have only a light dusting of sediment on their outer surfaces with a buildup of sediment along their sides (as much as 25% covered). While the shredded metal material in the bags was heavily coated with marine life (see figure 7-7), the can surfaces were only covered slightly by mussels and oysters. There was some biological activity inside the cans although not to the same extent, in either abundance or diversity, as was observed on the shredded materials (amphipods, bryozoans, limpids, scallops, annelids, clams, mussels, shrimp, barnacles, crabs, oysters, sponges, brittle stars, hydrozoans, radiolarians, and tunicates).

The presence of hydrogen sulfide smell and a blackening of materials inside the cans is indicative of oxygen utilization from degradation processes. This is most likely from degradation of food wastes (primarily) and the paper/cardboard inside the cans because of their oxygen demand. Corrosion of the metal would be an additional, although minor factor, in the oxygen utilization. The presence of foodstuffs inside the cans, a result of obtaining cans prepared for discharge ashore rather than for discharge at sea, is not expected to be a factor under normal discharge conditions. It is, thus, expected that the oxygen utilization would be substantially lower in normally discharged cans than was observed here.

The implications of this qualitative study are that the TDU cans do corrode relatively quickly in a shallow, relatively warm marine environment, as predicted. Under the conditions of high sedimentation, the cans will also get buried relatively quickly, as expected. While seawater leachates of these materials may have some toxicological effects to some test organisms, their presence on the sea floor does not exclude all biological activity. However, even exclusion of a species from the TDU container can only be considered an adverse condition if its effective surface area is sufficiently large relative to the areal extent of normal habitat. Although discussed in detail later within the context of mass loading to Special Areas, it can be safely assumed here that the amount of surface area of TDU containers on the sea floor relative to total sea floor will likely be insignificant.



Figure 7-7. Shredded metal and glass pieces coated heavily with marine life after about a year of sitting on the bottom of San Diego Bay (Chadwick et al., 1996).

### 7.3 BIOLOGICAL ANALYSES

A series of static-renewal EPA acceptable bioassays were conducted on some TDU cans and their contents to estimate the potential effects of the seawater elutriates described above on five organisms: mysid shrimp (*Mysidopsis bahia*); silverside minnows (*Menidia beryllina*); bioluminescent bacteria (*Photobacterium phosphoreum*); a marine chain diatom (*Skeletonema costatum*); and a marine dinoflagellate, (*Gonyaulax polyedra*). These tests were designed to look at the effects of the seawater soluble components of the TDU cans and their contents on a range of standard test organisms. Both chronic and acute tests were conducted where applicable. The work was primarily performed by MEC Analytical Systems, Inc. and their complete report can be found in Appendix A. The marine dinoflagellate (*G. polyedra*) toxicity test was performed in-house using the QwikLite Bioassay System (Lapota, 1994). A brief report on these tests is included in Appendix B. Where applicable, toxicological effects data for leachates of pulped paper and cardboard and for metals run as part of the surface ship work (Chadwick et al., 1996) will be also be summarized.

Bioassay organisms representing different phyla were chosen and tested where a toxic response found might represent a potential "risk" to the marine environment. *M. bahia*, a benthic shrimp, was chosen because it represents a species that is found both in the water column and on sediments, while the saltwater minnow, *M. beryllina*, was chosen to represent a pelagic or swimming species. The phytoplankton chain diatom species, *S. costatum*, and the dinoflagellate, *G. polyedra*, were used to observe any potential affect on primary producers in marine waters. The marine bacterium, *P. phosphoreum*, was used to test effects on these ubiquitous single cell



organisms. The endpoints measured were growth and survival for mysids and minnows, inhibition of luminescence in bacteria and dinoflagellates, and growth in phytoplankton. The dose-response tests provided a  $LC_{50}$ , that is the lethal concentration at which 50% of organisms were killed, and/or an  $IC_{50}$ , or  $EC_{50}$  which is the concentration at which 50% of organisms were inhibited, either in growth or in light output, by the test solution. In all cases, statistical analyses were also used to identify a No Observable Effects Concentration (NOEC) and a Low Observable Effects Concentration (LOEC).

The following is a brief summary of the methods that are described in the complete report within Appendices A and B. Each set of test organisms were subjected to decreasing concentrations of the elutriates under controlled laboratory conditions. The organisms were subjected to standard test concentrations of 100%, 50%, 25%, 12.5%, and 6.25% of the leachate by adding varying amounts of the test solution to clean, filtered seawater. The response of the organisms to these varying concentrations were then compared to control organisms not subjected to the test solution. Appropriate replicates were performed to provide statistical confidence in the results. The duration of the tests depended on the endpoint tested. *M. bahia* and *M. beryllina* were each tested over both a 96-hour period for survival (acute effects) and over a 7-day period for growth (chronic effects). *S. costatum* growth was tested over a four day period, a measure of chronic effects. *P. phosphoreum* was tested for light inhibition over 5 and 15 minutes (acute) and 22 hour period (chronic). *G. polyedra* was tested for light inhibition over 96 hours for an acute effects endpoint.

Initially, leachates of TDU4 and TDU5 with their contents of paper, cardboard, and a ballasting weight were analyzed for toxicity. Later in the study, leachates of containers TDU12, TDU13, TDU15, and TDU16 were analyzed for toxicity. Because these last four containers contained the complete suite of materials likely to be present in the waste stream, the following discussion will focus on these test results. Measurements of TDU12 and TDU13 were intended to represent replicates as were those of TDU15 and TDU16. Because of the variability in the replicate analyses and the discretized nature of the results, only the lowest bioassay result for each replicate will be discussed, thus, providing the most conservative view of the data. The  $LC_{50}$ ,  $IC_{50}$ , or  $EC_{50}$ , and LOEC, and NOEC test results were calculated using the test statistic appropriate for the raw test data and summarized in table 7-9. The full data set can be found in Appendices A and B.

The  $LC_{50}$  (survival) for both the mysid shrimp, *M. bahia*, and silverside minnows, *M. beryllina*, was greater than 50% in all cases while the  $IC_{50}$  (growth) was greater than 100%. These results indicate that the concentration of leachate needed to cause 50% mortality of these test organisms would have to be greater than 50%. Those organisms surviving the acute effect appear to live and grow at rates no different than organisms not subjected to the leachate. The lowest  $LC_{50}$  was observed for *M. bahia* in TDU15, which was from the can containing the elevated copper concentration. Standardized tests on control organisms indicated that the  $EC_{50}$  for copper sulfate was 60 ppb, suggesting that the low  $LC_{50}$  observed for TDU15 was likely a result of the anomalously high copper in the leachate. There was not a clear trend for differences in the leachates made with or without oily paper towels.

The Microtox® bioassays on the bacterium *P. phosphoreum* indicated  $EC_{50}$  values of greater than 74%, suggesting that the stress on these organisms (light inhibition) was relatively low. The lowest value was again associated with TDU15 although the effect of copper on these organisms was not specifically tested. There was not any difference between the two groups of TDU cans,

Table 7-9. Bioassay test results for seawater leachates of containers TDU12, TDU13, TDU15, and TDU16. Only the lowest value for each set of replicates is shown.

Paper, Cardboard, Metal, Glass Only (TDU12 and 13)	End Point	LC <sub>50</sub> , IC <sub>50</sub> , or EC <sub>50</sub> (% Leachate)	LOEC (% Leachate)	NOEC (% Leachate)
<i>Mysidopsis bahia</i>	Survival	>100	6.25	<6.25
<i>Mysidopsis bahia</i>	Growth	>100	100	100
<i>Menidia beryllina</i>	Survival	>100	6.25	<6.25
<i>Menidia beryllina</i>	Growth	>100	>100	100
<i>Photobacterium phosphoreum</i>	Light Output	81.9	-	-
<i>Skeletonema costatum</i>	Growth	3.6	6.25	<6.25
<i>Gonyaulax polyedra</i>	Light Output	4.3	6.25	<6.25

With Oily Paper Towels (TDU15 and 16)	End Point	LC <sub>50</sub> , IC <sub>50</sub> , or EC <sub>50</sub> (% Leachate)	LOEC (% Leachate)	NOEC (% Leachate)
<i>Mysidopsis bahia</i>	Survival	53.1	100	50
<i>Mysidopsis bahia</i>	Growth	>100	50	25
<i>Menidia beryllina</i>	Survival	56.6	12.5	6.25
<i>Menidia beryllina</i>	Growth	>100	>100	100
<i>Photobacterium phosphoreum</i>	Light Output	90.2	-	-
<i>Skeletonema costatum</i>	Growth	4.1	6.25	<6.25
<i>Gonyaulax polyedra</i>	Light Output	3.8	6.25	<6.25

i.e., those with and those without oily paper towels. The lack of significant toxicity differences for samples with and without oily paper towels results from the negligible amount of solubilized oil in the leachates and the relatively low toxicity of lubricating oil in general. Lubricating oils do not generally contain toxic low-molecular-weight or aromatic constituents. This combined with a low starting concentration of oil in the towels (18% to 40% by weight) and a very low solubility of lubricating oil in seawater, resulted in a lack of measurable toxic constituents in the priority pollutant scans and negligible difference in the toxicity results.

The relatively low IC<sub>50</sub> concentrations of about 4% for the two phytoplankton species, *S. costatum* and *G. polyedra*, indicate that these test organisms are the most sensitive to the TDU leachates. These species also tended to be the most sensitive in leachate tests with shredded metal components and pulped paper (Chadwick et al., 1996). The IC<sub>50</sub> values were similar for both species and for each leachate, regardless of the presence of oily paper towels or not. The relatively high copper concentrations seen in the leachate of TDU15 did not appear to cause a larger effect for *S. costatum*. The bioassays on *G. polyedra* were performed only on TDU12 and TDU16, and the effects of the higher copper were, therefore, not tested.

Bioassays performed on portions of the waste stream, either paper/cardboard, shredded metal components (Chadwick et al., 1996), or the TDU cans containing only paper and a ballasting weight, showed relatively less effects than those of the combined waste stream. The lowest NOEC value previously found for partial components was 6.25%, which provided a lower bound on the leachate concentration that causes effects in test organisms. However, for most bioassays of the combined waste stream, the lowest test concentration still caused an effect and, thus, the NOEC was not measured. In those instances where a NOEC was determined, the ratio of the LC<sub>50</sub>, IC<sub>50</sub>, or EC<sub>50</sub> to NOEC can be computed to provide a rough idea of what the NOEC might be in instances where it was not actually determined. Although quite variable, the ratio is

typically less than 10, suggesting that a 10:1 dilution of the lowest leachate concentration causing an effect would provide a NOEC for all test species. This implies that a leachate concentration of 0.4% should be below effects levels for all tested organisms.

As mentioned previously, containers TDU14 and TDU17 were placed in San Diego Bay and allowed to leach over a 24-hour period. Seawater samples were taken *in situ* by divers using a syringe to pull seawater from inside the container and from 50 cm away from the container surface. These *in situ* leachates were used as test solutions with *G. polyedra*, one of the more sensitive test species, as a comparison measure of toxicity to the standard laboratory analyses. Results of the bioassays run on the samples taken from inside the containers showed significantly lower toxicity than comparable laboratory leachates.  $IC_{50}$  values were about 15 times higher for the *in situ* samples than the laboratory leachates (64% versus 4%). While a NOEC value for the laboratory tests was not found (i.e., <6.25%), the *in situ* leachate samples had an NOEC value of 25%. Samples taken at 50 cm away from the containers showed no measurable toxicity with an  $IC_{50} > 100\%$  and NOEC values of 100%.

## 8.0 FATE AND EFFECTS ANALYSIS OF SUBMARINE SOLID WASTES

The fate and effects of solid waste discharges from U.S. Navy submarines as outlined in the conceptual model are discussed in this section. A TDU container with its contents of compressed paper, metal, glass, oily paper towels, and steel weights is discharged as a single unit. The package sinks quickly through the water column and is deposited onto the sea floor with relatively minor lateral transport by currents and only short term exposure to water column organisms. Once the container reaches the sea floor, it will tend to stay in place except under very strong current conditions. It is thus anticipated that most of the processes which influence the fate and effects of the waste will occur at or near the sediment water interface. These processes include burial, degradation, corrosion, and possible transport along the bottom by currents. Potential detrimental effects include physical damage and toxicity to benthic organisms, ingestion by benthic deposit feeders, and oxygen uptake during corrosion and degradation processes.

In many ways the fate and effects of this waste stream are similar to that analyzed previously for the shredded metal and glass waste stream discharged in burlap bags from surface ships (Chadwick et al., 1996). Like the burlap bags, individual components of the waste stream are unlikely to be dispersed over large areas, although the individual TDU containers will. Thus, the impacts of a single container will be the scale of importance from a fate and effects standpoint. Where applicable, the analysis developed for the fate and effects of surface ship solid waste discharges will be used. This will include an assessment of localized areas of impact related to a single container as well as an evaluation of potential basin-wide impacts using reasonably foreseeable estimates of loading and conservative measures of physical and ecological response. The multi-ship scenario used previously in Chadwick et al. (1996) is not applicable for submarines and will not be considered here, however, additive effects with surface ship discharges will be discussed.

### 8.1 DISCHARGE CONDITIONS

**Discharge Rates.** A best estimate of the amount of solid waste generated and discharged from submarines is derived from the submarine waste management study (NNS, 1994). As described previously in Section 6.1, the measured solid waste generation of about  $0.5 \text{ kg} \cdot \text{person}^{-1} \cdot \text{d}^{-1}$  of paper, cardboard, metal, glass, and oily paper towels (NNS, 1996) with a typical complement of 130 would produce approximately  $67 \text{ kg} \cdot \text{d}^{-1}$  of material required for daily disposal.

**Discharge Distribution.** The TDU is designed to handle multiple containers per discharge. With three containers a day and normal operational requirements for speed, noise, and safety, the TDU is likely utilized only once daily. Even though the submarine is required to travel at speeds less than 5 knots during discharge, it is unlikely that the containers will remain next to each other once they reach the sea floor. Hence, the amount of sea floor impacted from a discharge can be estimated to be equivalent to the dimension of a single container having a rough rectangular base of 23 by 60 cm, which has a footprint of roughly  $1400 \text{ cm}^2$ . If the can were to sink completely into a soft sediment, the full can surface area of  $5165 \text{ cm}^2$  could potentially be in contact with the sea floor.

Current discharge regulations imposed by OPNAVINST 5090.1B restrict discharges from submarines to greater than 12 nmi from shore if the water depth exceeds 1000 fathoms or

1829 m. Discharges are allowed at greater than 25 nmi from shore in all water depths. These restrictions imply that for most areas of the world, submarines will be discharging into deep water environments. This is not necessarily true for some Special Areas. The Persian Gulf, North Sea, and the Gulf of Mexico all have large expanses of shallow-water environments. It is in regions of shallow water where sensitive biological endpoints are expected to be present, or conversely, deep water environments typically do not have sensitive ecological endpoints (Merkel et al., 1996). In this way, current operational guidelines already minimize the areal distribution for potential impacts of waste discharges.

## 8.2 WASTE STREAM CHARACTERISTICS

**Sinkability.** The design of the TDU container promotes its quick descent to the sea floor. Its size, weight, and permeable construction enables rapid settling through the water column. Although settling experiments on non-weighted containers suggest that some cans needed to be purged of air to sink, the addition of weights to the container, as required by TDU system manuals, ensures sinking. For example, one steel weight (~2.5 kg) is sufficient to counteract buoyancy produced by trapping as much air as 10% of the container volume. With an average settling velocity of fully weighted cans of  $133 \text{ m} \cdot \text{min}^{-1}$ , even the deepest regions of Special Areas of approximately 4000 m, will be reached in only 30 minutes. The obvious implications of this are insignificant exposure in the water column and minimal potential for lateral transport.

**Container Integrity.** Even though the containers fall through the water column at a relatively high rate, the tests conducted in this study, albeit under only one bottom condition, indicate that they are unlikely to break open either on descent or upon impact with the bottom. The integrity of the container dropped multiple times onto a hard, sandy bottom suggests that the contents will likely remain within the container until the can disintegrates as a result of corrosion. The most probable exception to this might occur over a rocky sea floor, which was not tested. This implies that the wastes, other than small particulates, will be unavailable for ingestion by water column organisms or by benthic macro-organisms until the can corrodes, and its contents are more openly exposed.

**Chemical Composition.** The waste stream is composed of a mixture of organic and inorganic constituents in roughly equal proportions. Paper and cardboard are primarily composed of cellulose, which is an organic material that degrades through natural microbial degradation processes. Inorganic components including the metal wastes from crushed tin-coated steel and aluminum cans, the steel weights added for sinking, the metal container itself, and glass degrade through natural chemical processes.

As was previously shown in table 6-2, the major bulk constituent of a typical package is paper and cardboard, making up about 43% of the package. However, the container, metal weights, and added metal waste make up a combined 46% of the package. Thus, the overall package can be characterized as roughly 43% organic matter, 46% metal, with the remainder approximately 7% glass and 4% oily paper towels. These bulk constituents can be broken down into their elemental components using results of the chemical analyses performed as part of this study as well as the previous surface ship solid waste study (Chadwick et al., 1996). This is done by multiplying the elemental compositions of each item by its percentage represented in the total package. In some instances the exact elemental composition is available (e.g., for metals) while in other instances (e.g., for glass), only a relative breakdown of the most common oxides is available. Furthermore, only elements making up greater than 0.5% by weight of the bulk

constituent are considered in the analysis, and oily paper towels were not broken down into their elemental constituents. The results of these calculations are shown below in table 8-1.

The two primary elements that make up the TDU package are iron and organic carbon. They each are about 45% of the total waste stream by weight, similar to the percentages of the bulk constituents from which they are derived. The next most abundant elements are the oxides of silicon, sodium, and calcium. The remaining elements are found at an abundance of less than 0.5% of the total. Elemental iron forms an oxide in seawater and is found in relatively high abundance in deep-sea sedimentary materials (see table 8-1). Although typically found at a concentration of roughly 6% in deep-sea clays (Chester, 1990), its abundance can vary from 0.9% in deep-sea carbonates to over 14% in ferro-manganese nodule deposits (Chester, 1990). Thus, the waste package is enriched in iron relative to concentrations found in typical sedimentary materials. The enrichment is a factor of almost 8 relative to deep sea.

Table 8-1. Elemental composition of materials making up a typical TDU container and its contents, and a comparison with that of deep-sea clays (Chester, 1990).

Element	Amount in TDU Waste Package (kg)	Percentage in TDU Waste Package (%)	Percentage in Deep Sea Clays (%)	Ratio TDU/Clays
Fe	12.6	47.54%	6.0	7.9
Org C	11.4	42.91%	0.3	143.0
Si (oxide)	1.6	6.23%	55.0	0.1
Na (oxide)	0.28	1.05%	1.5	0.7
Ca (oxide)	0.22	0.83%	0.9	0.9
Al	0.13	0.48%	10.0	0.05
Ti	0.11	0.41%	0.6	0.7
Mn	0.06	0.23%	0.6	0.4
Sn	0.06	0.22%	0.0002	1100.0
Cu	0.02	0.09%	0.2	0.5
Mg	0.002	0.01%	2.0	0.005
Total	26.57	100.00%	77.0	-

The organic carbon content of marine sediments can vary significantly as a consequence of local sources. The main source of organic carbon in the ocean is *in situ* photosynthesis by phytoplankton. Terrestrial sources from riverine input and atmospheric deposition are other sources of organic matter to the sea. As such, geographic location, both from a primary productivity aspect and nearness to shore, play a role in how much organic carbon eventually gets deposited into sediments. Carbohydrates in general, and cellulose in particular, are common components of the organic matter incorporated into marine sediments (Chester, 1990). Typical concentrations of organic carbon found in deep-sea sediments are about 0.2-0.3% by weight (Chester, 1990) while near-shore sediments can be as high as 18% (Sverdrup et al., 1942). The TDU package, therefore, is enriched in organic carbon content relative to concentrations found in typical sedimentary materials by a factor of nearly 150 (table 8-1). Compared to near-shore sediments, however, the enrichment might be only be a factor of two.

Although not in great abundance in the TDU waste stream, elemental tin is highly enriched (factor of 1100) relative to typical marine sediments. Tin in the TDU package is derived from the protective coating applied to the steel food containers disposed in the waste stream. Thus,

even though the coating of tin applied to the cans is less than 0.06 mil, the amount is still anomalous relative to background materials.

**Priority Pollutant Chemicals.** The priority pollutant scans made on seawater elutriates of the TDU container waste stream indicate that the only compound measured consistently is zinc. However, the concentration of zinc observed was well below the WQC set by EPA. Other compounds observed occasionally in leachates of some containers or of individual waste stream components have included copper, phenols, phthalates, acetone, or hydrocarbons. Of these, only copper in one sample was observed at a level clearly above WQC set by the EPA. The remaining compounds do not have WQC set by the EPA. However, minimum chronic effects concentrations for phthalate esters of 3.4 ppb (U.S. EPA, 1987) were surpassed in two separate samples by a single phthalate ester.

To apply these chemistry results to real-world effects requires some estimation of what the effective concentration field might be in and around the TDU container once it is deposited onto the sea floor. The real-world analogue of the elutriate can be thought of as a stagnant volume of seawater into which the TDU package leaches. This analogy is conservative because there is constant diffusion and almost always an advective field that serve to dilute concentrations in the sea. The effective concentration of a leached contaminant can be calculated using an idealized container geometry of a half sphere lying on the sediment surface and computing concentric volumes and, hence, concentration as a function of distance from the container surface. This provides an estimate of the concentration gradient that likely will exist in the real-world.

The results of this analysis for copper and phthalates are shown in figures 8-1 and 8-2. A starting concentration of 191 ppb copper inside the container would dilute to a value less than the EPA WQC value of 2.9 ppb within a distance of 70 cm (figure 8-1). This suggests that the copper concentrations at a distance of >70 cm from the container would be below a level considered potentially harmful. As previously discussed in Section 7.2, the presence of copper at 191 ppb is considered anomalous source for TDU cans in general. Similarly for the phthalates, a concentration value of 15 ppb would drop off below the lowest effects guideline within 15 cm of TDU container surface (figure 8-2).

**Degradability.** Alteration of the container and its contents proceeds as a result of natural chemical and microbially mediated processes once the material is discharged into the marine environment. These processes modify the physical and chemical makeup of the waste stream constituents and help to redistribute them partially through dissolution and remineralization in other forms. These are also mechanisms for changing the aesthetic nature of the waste stream from one that is clearly a component of anthropogenic litter to one that may not be recognizable as anything different from typical sedimentary materials.

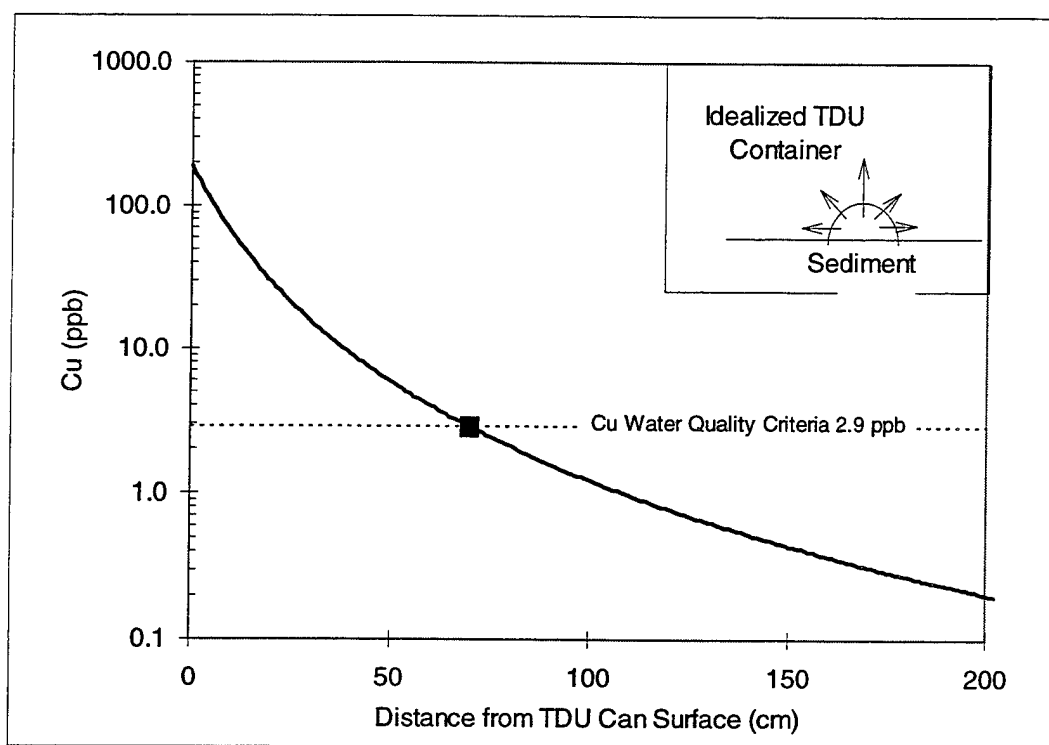


Figure 8-1. Copper concentration as a function of distance from an idealized TDU container surface. The modeled copper concentration decreases below the WQC of 2.9 ppb at a distance of 70 cm from the container.

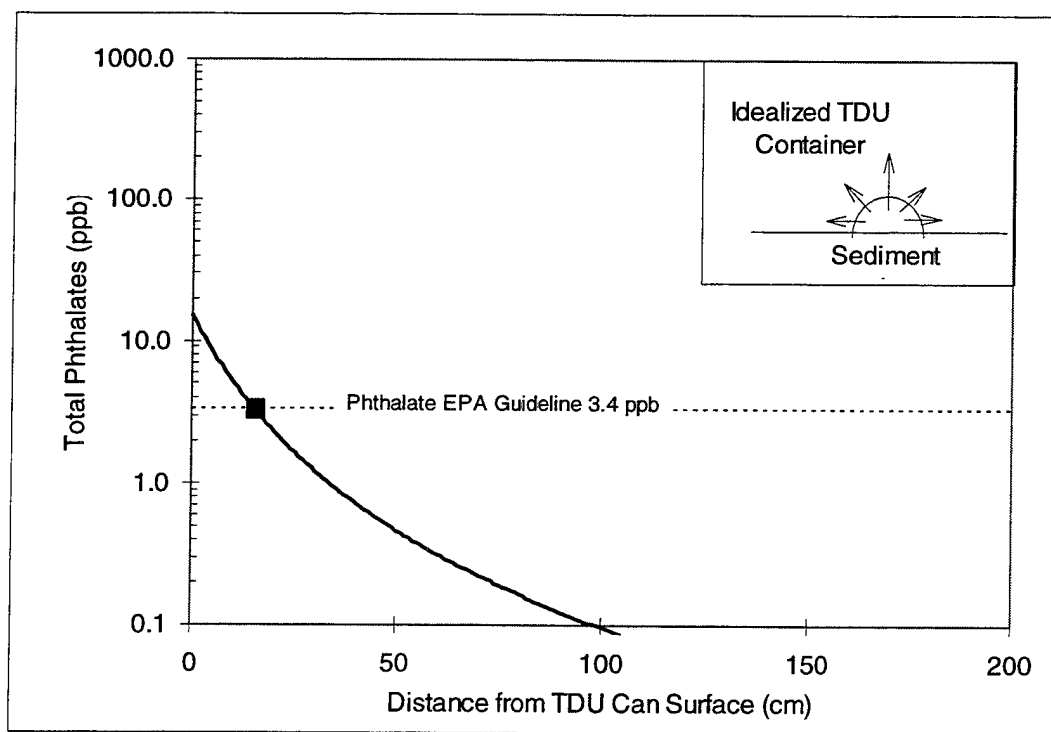


Figure 8-2. Phthalate ester concentration as a function of distance from an idealized TDU container surface. The modeled concentration decreases below the EPA guideline 3.4 ppb at a distance of 15 cm from the container.



Microbial degradation rates for pulped paper and cardboard were determined on both pulped and non-pulped paper and cardboard. The results of these analyses suggest that the non-pulped cellulose material will initially degrade more slowly than the pulped material but should eventually (30 to 60 days) reach rates comparable to those for pulped material. This implies that the rates determined from the more extensive testing of pulped paper and cardboard would be applicable to the contents of TDU's. The maximum degradation rate for pulped material was  $0.5\% \cdot d^{-1}$  under warm ( $28^{\circ}C$ ), non-nutrient limited conditions, for example, conditions such as those that might be found in the shallow waters of the Mediterranean Sea. Under cold ( $4^{\circ}C$ ), non-nutrient limiting conditions, such as those that might be found in the bottom waters of the Caribbean, the rates decrease to  $0.043\% \cdot d^{-1}$ . This suggests that the half-life of the cellulosic material in the TDU's would range from about 200 or so days in warm waters to over 2300 days (6.4 years) under cold water conditions. The time required to degrade to near completion (95%) would be between 1.6 and 19 years.

Corrosion rates were not experimentally determined in this study. Rather, the metal portion of the waste stream was characterized in terms of material types and amounts in order to estimate a likely range of expected corrosion times using literature rates. Although the materials were characterized fairly well, corrosion rates are highly dependent on the receiving environment, particularly on ocean parameters such as oxygen, pH, temperature, pressure, and biofouling. Because the receiving environments of Special Areas span the full range of possible conditions found in the sea, corrosion rates will span a large range. Likely rates were estimated to be 0.6 to 11 mpy for steel components and 0.1 to 3.9 mpy for aluminum components, with typical rates of 2 mpy and 1 mpy, respectively. The protective tin coatings of the steel cans were predicted to have an insignificant effect on these corrosion rates.

Based on the 2 mpy corrosion rate on each side, the TDU containers are estimated to have a lifetime in the range of 1 to 16 years. The iron weights are expected to have a 190 (35 to 635) year lifetime. The tin-coated steel cans were estimated to have a lifetime of 2.5 (0.5-8.5) years while aluminum cans were estimated to have a 10 (2.5-100) year lifetime. These estimates suggest that the materials may be transformed very slowly and be incorporated into the sedimentary record at least partially intact.

Maximum corrosion rates will typically be found for warm water, high oxygen conditions, which are common in shallow-water environments. Because of discharge restrictions, TDU containers will typically be discharged into the deeper portions of Special Areas and the oceans. The implication is that for the most part, they will be discharged into colder waters that will typically have lower corrosion rates. Exceptions to this in Special Areas are for the Gulfs Area which is almost all shallow and warm, and for the Red Sea, which is warm even in its deep regions. It would, therefore, be expected that the majority of containers would be discharged into water conditions that promote slower corrosion. This suggests that, in general, the containers will remain intact with their contents for reasonably long time periods.

A gross estimate for the amount of oxygen utilized to completely oxidize the metal components of the waste stream is 0.75 mole  $O_2$  per mole Fe (see Appendix G of Chadwick et al., 1996). With roughly 12.5 kg of Fe ( $56 \text{ g} \cdot \text{mole}^{-1}$ ) available in each package, the amount of  $O_2$  used would be approximately 225 moles  $O_2$  per container. The effect of oxygen demand from corrosion will be considered later under basin-wide scenarios.

Degradation of the glass waste stream will occur mainly through the dissolution of its constituent oxides. The susceptibility of glass to fatigue fracture under static loading may also lead to physical degradation as well as an enhanced solubilization of silica within the fractures (Glass Products and Production, 1974), particularly at greater depths. Dissolution of glass, mainly  $\text{SiO}_2$ , will occur because the world's oceans, including Special Areas, are undersaturated with respect to silica. The time constants for these reactions, although poorly known, are exceptionally long, which can be attested to by the fact that there are large silicon-rich deposits distributed throughout much of the world's oceans when, theoretically, there should be no Si present. In general, Si-rich sediments are found underlying regions of high primary productivity where the flux of siliceous material to the sea floor is high and where burial rates are high. This suggests that the kinetics of reaction are sufficiently slow enough, relative to burial rates, to allow the material to become incorporated into the sea floor. It is, therefore, likely that any input of glass from the waste stream will be incorporated into the sea floor in a state not much different than its original form.

**Biological Effects.** Effects of the TDU container and its contents on marine organisms were addressed using bioassay toxicity testing. Determination of contaminant concentrations alone offers little insight into predicting adverse biological effects because bioavailability of a contaminant may limit its potential for effects while multiple contaminants may increase the potential for synergistic effects. Because of this, toxicity tests have evolved into effective tools that provide direct, quantifiable evidence of biological consequences of contamination (U.S.EPA, 1994).

Results of bioassay tests conducted on seawater leachates of the complete TDU waste stream (section 7.3) suggest that some toxic effects were elicited in some test organisms. The same was true for test solutions made from seawater leachates of pulped paper and cardboard and of shredded metal materials. A range of adverse responses including mortality, growth, or light inhibition were tested on a variety of organisms representing bacteria, phytoplankton, invertebrates, and fish. However, the results observed in these laboratory tests need to be assessed in relation to actual exposure levels expected under real-world conditions in order to understand their true potential for impacting the marine environment.

Laboratory toxicity results can be extended to estimated real-world effects in two ways. In similar fashion as was done for the chemistry results, the leachate concentration field can be modeled using an idealized container geometry of a half sphere lying on the sediment surface, and assuming dilution occurs in an increasing volume as a function of increasing distance away from the container surface. Results of this calculation are shown as the smooth line dilution curve in figure 8-3. Based on this curve, a concentration equivalent to the lowest observed laboratory  $\text{IC}_{50}$  of about 4% for both *S. costatum* and *G. polyedra* would be reached at a distance of about 44 cm from the container surface. Based on this model, a leachate concentration of 0.4 % would be reached at a distance of 122 cm from the container surface. This concentration value is the expected NOEC for all species based on an approximation that the  $\text{IC}_{50}$ /NOEC ratio of about 10 calculated for the bioassays in which both values were measured, holds true for the most sensitive tests in which only an  $\text{IC}_{50}$  was measured.

A second way to extend the laboratory toxicity results to real-world estimates is to use the results of the *in situ* leaching tests. These results, when plotted on the same dilution curve shown in figure 8-3, indicate that the above estimates are conservative. The measured  $\text{IC}_{50}$  value of 64% for the *in situ* leachate taken from inside the containers and tested on the most sensitive species

*G. polyedra*, plots onto the curve at a distance less than 5 cm from the can surface. The NOEC of 25% for the *in situ* leachate taken from inside the can would be reached at a distance of about 13 cm from the TDU surface. This indicates that the measured toxicity effects from *in situ* leachates are considerably lower than the leachates generated in the laboratory, ostensibly because of the real-world dilution effects. This estimate is also supported by the measured *in situ* sample taken at 50 cm from the TDU can surface for which there were no measured toxic effect. Given that there may be some toxic effects to some organisms by the TDU waste container, they appear to be confined to the immediate vicinity of the container. The worst case is that toxicity falls off to a no effects level within a distance of 122 cm of the TDU can while the likelihood, based on the *in situ* leachates, is that toxicity would fall off to no effects within 13 cm of the can surface.

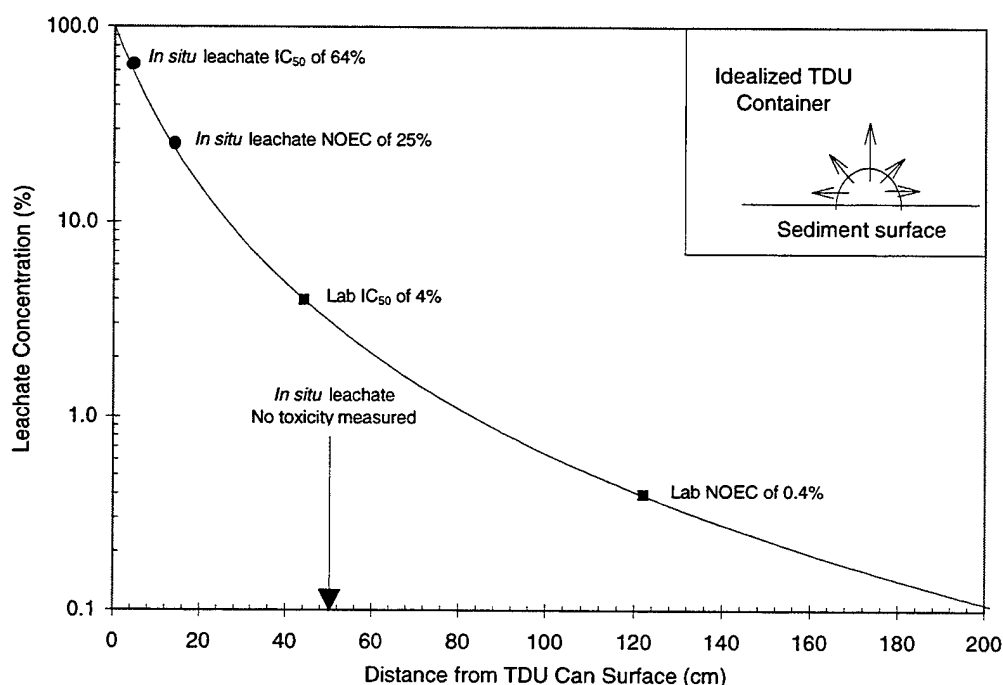


Figure 8-3. Leachate concentration as a function of distance from an idealized TDU container surface based on dilution. The concentration decreases below the lowest measured IC<sub>50</sub> value of 4% at a distance of 44 cm. The concentration also decreases below an estimate of the lowest NOEC expected for all species (0.4%) at 122 cm. Results of the bioassays using the *in situ* leachates are also plotted for comparison.

**Long Term Studies.** Another indicator of potential biological effects from the TDU can comes from the long-term *in situ* study. After 225 days on the sea floor of San Diego Bay, minimal growth was observed on TDU container surfaces and moderate biological activity was seen inside them. It is expected that over even longer periods of time that they would become further colonized with a variety of organisms, as was observed for the burlap bags full of shredded metal and glass similarly deployed. There is plenty of evidence of this phenomenon in the marine environment, including fouling of pier pilings and sunken ship hulls. The addition of these surfaces to the marine environment will typically serve as good substrates for recruitment

and growth. How abundant and diverse the growth will be is dependent on the surrounding seawater conditions, including temperature, oxygen, nutrients, and the presence or absence of organisms. Although the materials were shown to have an impact on some sensitive organisms under prescribed laboratory conditions, these results suggest that there are many other organisms that are not adversely affected by them.

### 8.3 WATER COLUMN PROCESSES, FATE, AND EFFECTS

Because the TDU cans sink quickly through the water column, the time scale of processes that might affect the water column will be quite limited, ranging from seconds to minutes. The processes likely to be important in the water column are, therefore, confined to lateral transport and the potential for the materials to impact the coastal zone as shore litter. Unless the cans break open, which has been shown to be unlikely, the exposure time to organisms in the water column is likely too short to be of consequence. The following discussion, thus, focuses on lateral transport, its consequence on the distribution of cans reaching the bottom, and their potential for reaching shore.

**Lateral Transport.** Lateral transport of the cans during descent is strictly a function of water current speed and water depth because estimates of the hydrodynamic drag on the can suggest that it becomes fully entrained in the current flow almost immediately. Also, any momentum imparted by the foreword motion of the ship would be quickly dissipated when the can enters the water. Using the average sink rate of  $133 \text{ m}\cdot\text{min}^{-1}$  and a nominal current condition of  $50 \text{ cm}\cdot\text{s}^{-1}$ , the lateral displacement of the cans in water depths of 50 to 4000 m, which are typical depths found in the North Sea and Antarctic, for example, would be 11 to 1140 m from the drop point. These numbers would obviously change under differing flow conditions. Higher flows of up to  $150 \text{ cm}\cdot\text{s}^{-1}$  may be found in near-surface waters as a result of wind-driven conditions, such as those found in the Baltic Sea, or in constricted regions with tidal current flows up to  $200 \text{ cm}\cdot\text{s}^{-1}$ , such as those found within narrow straits of the Mediterranean (Defense Mapping Agency, 1988 and 1990). Maximum displacement in the Baltic under these flow conditions would be about 310 m using its maximum depth of 460 m. In the Mediterranean case, the high flows tend to occur in locations that are typically less than 500 m in depth and, thus, the displacement would be roughly 450 m. In both cases, the lateral transports are still reasonably small because the transport occurs over a short time interval. Although lateral transports are higher in these high-flow areas, their likelihood of occurrence is much lower because of their limited spatial and temporal distribution within Special Areas.

**Areal Distribution.** The effect of lateral transport increases the potential areal distribution of cans impacting the bottom from a single ship discharge. The dispersal of cans away from a ship's trackline would serve to minimize the density of cans on the bottom in a given area by effectively increasing the swath width of the discharge. Thus, the most conservative estimates of surface area coverage would be based on the assumption of no lateral transport.

**Coastline Impacts.** Another aspect of transport is whether or not the cans are likely to reach the shoreline following discharge and become a coastal litter issue even though there is no evidence that submarine discharges have ever reached shore, and these discharges have occurred since the 1950s. While this aspect of transport cannot be readily treated in a numerical computer simulation because of grid size limitations, it can be approached using measured settling rates, simplified bottom topography, current speed, and discharge distance from shore. Discharge distance from shore was considered for the two limits imposed on submarine discharges, 12 and

25 nmi (22.2 and 46.3 km). The depth limit of >1000 fathoms (1830 m) required for discharges between 12 and 25 nmi was considered as well. Bottom topography was assumed to slope linearly from the discharge limit depth to a depth of 0 m at the shore. In the case of the 12 nmi limit a discharge depth of 1830 m was used, creating a bottom slope of about 8%, which is substantially higher than the average continental slope value reported by Sverdrup et al. (1942). For the 25-nmi limit, a depth of 200 m was used, which is reasonable, based on a review of Special Areas bathymetric charts. This scenario results in a bottom slope of about 0.4%, which is comparable to values reported by Sverdrup et al. (1942).

Using the above conditions, depositional depths and depositional distances from shore were estimated using onshore current velocities ranging from 0 to  $100 \text{ cm}\cdot\text{s}^{-1}$  and the average TDU container settling velocity of  $133 \text{ m}\cdot\text{min}^{-1}$  (figure 8-4). The results for discharges at the 12-nmi limit show that for a typical current speed of about  $50 \text{ cm}\cdot\text{s}^{-1}$ , the can would be deposited in 1795 m of water, 21.8 km from shore, having moved shore-ward 0.4 km. At the highest onshore velocity examined ( $100 \text{ cm}\cdot\text{s}^{-1}$ ), the can would be deposited in 1765 m, 21.4 km from shore, having moved shore-ward about 0.8 km. For the 25-nmi (46.3-km) limit, the cans will be deposited at water depths very similar to those at which they are discharged, e.g., if cans are discharged in water depths of 200 m, they will be deposited in a water depth of roughly 199 m (figure 8-5). The containers will also only be displaced a maximum of about 100 m. From this analysis it can be safely assumed that if the TDU cans are discharged outside the distance-from-shore limits under typical shelf-flow conditions, they will not be a source of coastal litter.

In summary, water column processes will not play a significant role in the fate and effects of the TDU waste stream. The high sinking velocity minimizes the time TDU cans spend in the water column, which in turn limits the potential lateral or shore-ward transport of the cans. Discharge of the TDU waste stream outside the 12 or 25 nmi limits will preclude this waste stream from becoming a source of coastal litter.

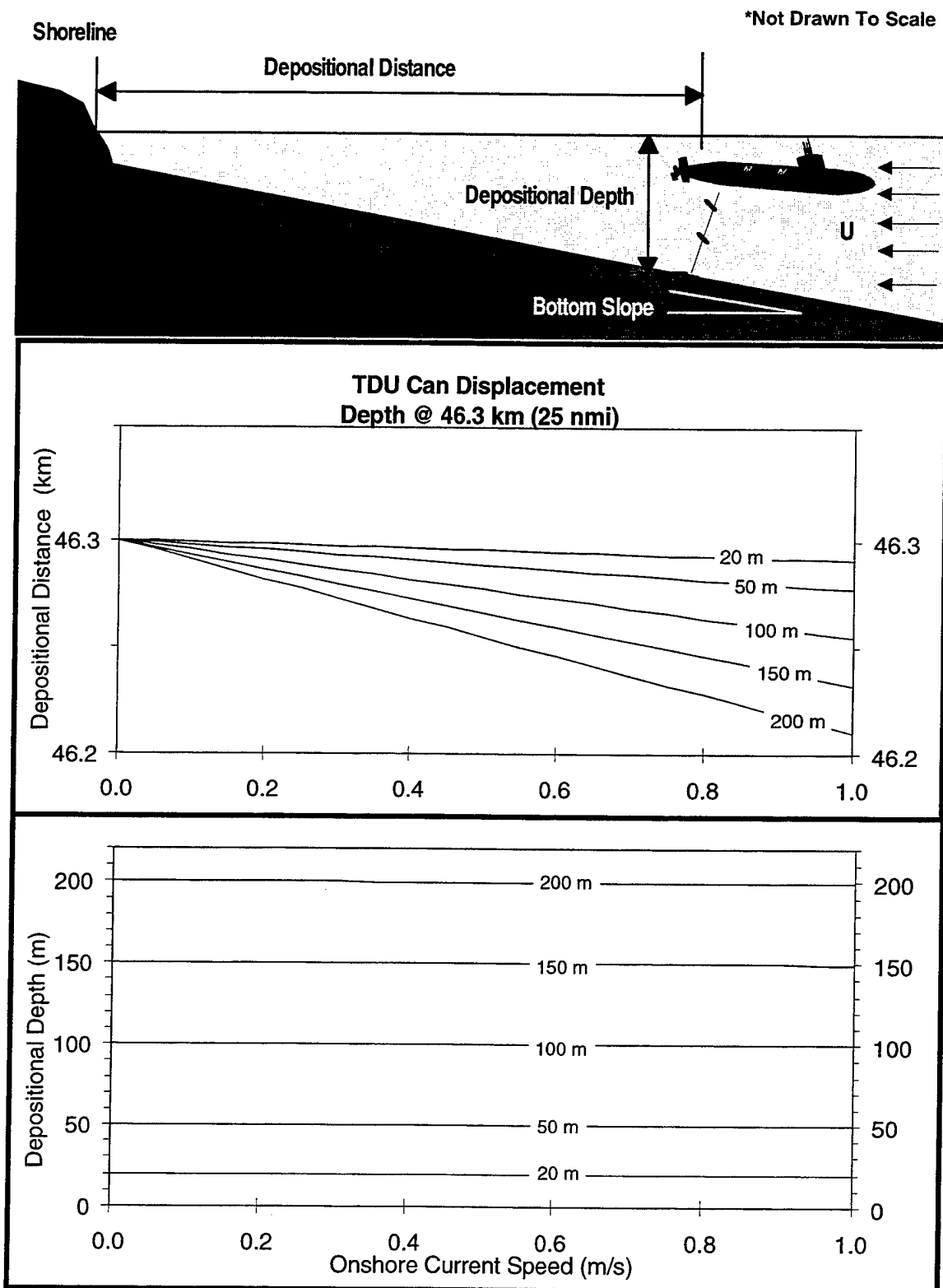


Figure 8-4. Pattern of TDU can discharge deposition at various depths and distances for the 46.3-km (25-nmi) discharge case. Shown are the depths and distances from shore of TDU can discharge deposited under a range of onshore velocities and initial bottom depths. \*Note, diagram is not drawn to scale; TDU cans are shown relatively larger than actual.

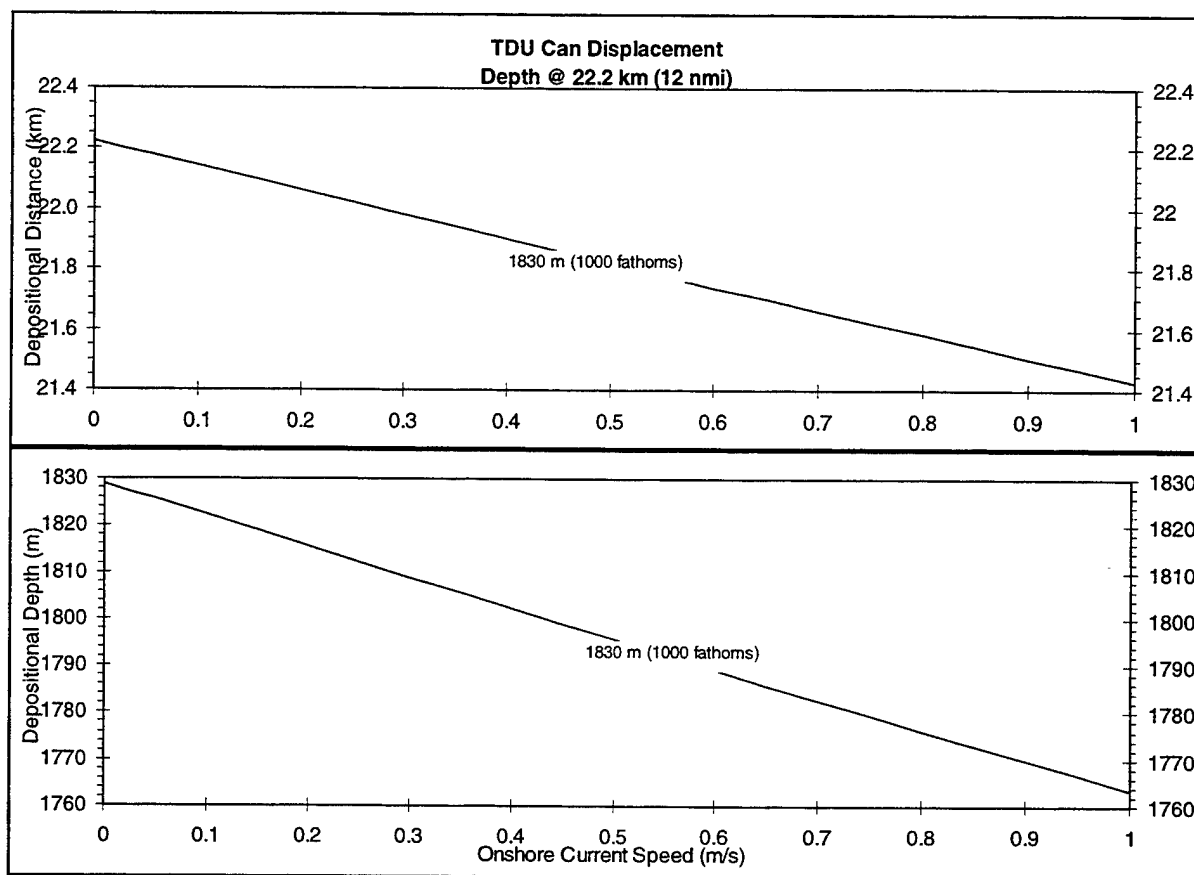


Figure 8-5. Pattern of TDU container discharge deposition at various depths and distances for the 22.2-km (12-nmi) discharge case. Shown are depths and distances from shore of TDU containers deposited under a range of onshore velocities assuming a discharge depth of 1830 m (1000 fathoms).

#### 8.4 SEA FLOOR PROCESSES, FATE, AND EFFECTS

**Fate on the Sea Floor.** The fate and effects of the TDU waste stream package on the sea floor will be controlled by the conditions of its depositional environment. For MARPOL Special Areas, these conditions cover the full spectrum of those found anywhere in the world's oceans. Processes dictated by the depositional environment include burial, corrosion, degradation, and transport. These processes tend to modify impacts from both a biological effects and aesthetics point-of-view. Understanding these processes, as well as the physical and chemical nature of the waste stream, provides a basis for assessing the fate and effects of the solid waste package in the ocean. The ultimate fate of materials once discharged, is that they or their by-products of corrosion and degradation will remain forever within the sedimentary record.

Because of the discrete nature of the discharge, the TDU waste stream will be irregularly distributed on the sea floor. Based on discharge limits, the packages are more likely to find their way into deep-water environments rather than into shallow-water areas. Processes on the sea floor will tend to redistribute these materials over time, eventually incorporating them into the sedimentary record. Burial of the TDU container by natural sedimentation will serve to redistribute and dilute it within the vertical sediment column over time. Similarly, the corrosion process solubilizes and transforms metal materials into smaller particles that enhance their

integration into the sediment column. Finally, transport processes will result in wholesale redistribution of the package, or in the case of breakage, any of its component parts.

Natural sedimentation rates represent the long-term difference between deposition and erosion and vary from about 1 to 20 mm·1000 y<sup>-1</sup> in the deep sea to greater than 1000 mm·1000 y<sup>-1</sup> on the shelf and coastal regions (Seibold and Berger, 1982; Kennett, 1982). Complete burial of the container at a sedimentation rate representative of the deep sea of 1 mm·1000 y<sup>-1</sup> would take nearly 240,000 years. For a sedimentation rate representative of the Baltic Sea (Voipio, 1981), burial would be completed in roughly 240 years. Remembering that the time scale for corrosion of the steel weights ranges up to 200 years, and cellulose degradation may occur over tens of years, one can see that if TDU cans are deposited into a region of low sedimentation, the processes of corrosion and degradation would control the fate of the materials. In high sedimentation rate areas, the process of burial would occur on a time scale more similar to that for corrosion and degradation. Thus, the balance of these rates will play an important role in how much and what form the material is incorporated into the sedimentary record.

Because of the container's large size, the process of bioturbation (Aller, 1980) discussion of small particles on the sea floor in Chadwick et al., 1996, is not applicable here. However, if a container breaks open, for instance, as a result of the corrosion process, individual pieces of the waste stream may be dispersed and eventually be integrated into the sediment column through both sedimentation and vertical mixing accelerated by bioturbation. This is also true for components of the waste stream that are degraded or corroded into smaller particles.

Given a time frame of about 1 to 16 years for corrosion of the TDU container itself and burial rates on the order of hundreds of years, it is likely that the contents of the can would eventually become more available for dispersion and biological interaction once the can corroded open. Use of a non-corroding material for the container would ensure that the waste stream materials would be buried intact under all conditions, except breakage. The benefit of this would be to minimize the likelihood that small to mid-size particles would be available to bottom foragers while a disadvantage would be that the materials would never be spatially distributed within the sediment column, a form of dilution. Neither of these are primary factors in the ultimate fate or impacts of these wastes on the sea floor. Thus, the use of a non-corroding container should have minimal impact from an environmental effects standpoint. Therefore, there is no appreciable environmental benefit to using a non-corroding container over the existing corroding container.

As discussed earlier, the elemental constituents of the waste stream that are significantly enriched over typical oceanic sediments are iron, organic carbon, and tin. Except for these constituents, the impact of the TDU waste stream does not significantly alter the general chemistry of surficial sediments. While not necessarily pleasing from an aesthetic point-of-view, the waste stream is composed of materials that are not dramatically different from those occurring naturally on the sea floor. The result is that a localized elevation of these elements will likely be maintained in the sedimentary record everywhere a TDU container is present. However, where corrosion and degradation can solubilize material at a higher rate than burial, the amount of enrichment will be minimized.

Under most bottom conditions, transport of the container along the sea floor is unlikely to occur. Although not measured, the current speed required to move the heavy package is expected to be anomalously high, especially if the can is deposited in the deep sea. The cylindrical shape of the



container would allow it to roll if there were conditions providing sufficient force. However, the amount of force required, or where this force might occur in the ocean, has not been studied.

**Exposure and Effects on the Sea Floor.** Possible adverse biological effects from discharging TDU containers into the marine environment, conceptualized earlier in figure 2-1, may include toxicological effects, physical damage from direct impact, and effects from ingestion. The potential for these impacts are discussed below using best estimates of potential exposure to sensitive biological endpoints. The estimates are based on typical conditions for discharge and knowledge of the receiving environments of Special Areas. The more sensitive biological endpoints considered include those with the most sensitive response in toxicity tests, coral reefs, and endangered species.

Laboratory toxicity test results are useful in understanding the potential effects on organisms in the field only when actual exposure (magnitude and duration) levels in the field are determined. When toxicity results were considered under a conservative real-world condition, it was estimated that an adverse response in the most sensitive test species might be elicited within a distance of 122 cm from the container. Measurements made *in situ* indicated that the more likely condition is that toxicity to these species might occur only when found within 13 cm of the container. The responses elicited in the two phytoplankton species included decreased growth rate or light inhibition after 1 to 7 day exposures. While the test durations were reasonable in light of the expected long-term fate of the TDU cans on the sea floor, exposure of these free-floating species would require that they maintain contact with the container. The most conservative view of potential toxicity effects is, therefore, that some organisms may be adversely effected when in very close proximity to the container. This is qualitatively confirmed by the long-term monitoring of TDU containers in San Diego Bay, which indicated that the material does not adversely affect all organisms coming in contact with it.

**Potential Impacts to Coral Reefs.** As a component of the NRaD shipboard solid waste assessment studies, the potential exposure and effects of solid waste discharges on coral reefs were examined (Katz et al., 1996). The coral reef assessment included the following primary objectives: (1) to determine the general distribution of coral reefs in MARPOL Special Areas; (2) to determine the extent of U.S. Navy surface vessel operations in areas where coral reefs exist; and (3) to evaluate, based on estimated exposure levels, the potential impact of U.S. Navy solid waste discharges on coral reefs in MARPOL Special Areas. The findings of this assessment and implications with regards to submarine discharges are discussed below.

Potential impacts to reefs from surface vessels considered both pulped and shredded waste streams. Potential effects from pulped materials included toxicity, reduction in light levels, smothering, and stress and mortality due to increased clearing requirements. Shredded wastes were considered for their potential for direct physical impacts from the burlap bags landing on coral reefs and subsequent smothering and shading. The potential for direct physical impact to coral reefs was, thus, an assessment of the likelihood that ship operations will place ships and their discharges on or near coral reefs in MARPOL Special Areas. Because of the discrete nature of TDU discharges, they are expected to have a similar potential impact to coral reefs.

Worldwide, coral reefs are generally distributed in tropical and subtropical regions between the latitudes of 30° N and 30° S. In general, coral reefs thrive in warm temperatures between 20° to 28° C and have evolved to require abundant light in shallower waters, typically 50 m, although some are found at depths up to approximately 200 m. The general distribution of coral reefs in

MARPOL Special Areas was determined based on published reports. The best available data sources for this information, digitized for use in this assessment, were found to be the reports developed by UNEP (1988) and the recently compiled "ReefBase" database (McManus et al., 1996). Of the eight existing and proposed Special Areas, only three have significant coral reef systems: the Red Sea, the Gulfs Area, and the Wider Caribbean Basin.

The extent of surface vessel operations within the specific Special Areas where coral reefs exist was determined using historical CNO EMPSKD data (OSD N311ND). The assessment considered two historical sources of information to identify vessel location data. First, port visit data were derived for the 1985 to 1994 time period to determine which ports were visited most frequently. Ports visited more frequently than 10 times per year and which had coral reefs in reasonable proximity to the port were considered for further analysis. Second, historical vessel movement data from the same time period were used to produce a relational database that could be used to collocate coral reefs and actual ship positions.

Exposure was considered by looking at the overlap of vessel locations with known coral reef locations. For port visit data, it was assumed that the vessels cross over the same path while entering and leaving port, that they discharge at the average daily rate while transiting into and out of port, and that the width of the shredder bag waste field was equivalent to the beam for each ship class. Based on the maximum number of yearly port visits (Roosevelt Roads in the Wider Caribbean Area), even if all visiting surface vessels discharged directly over coral reefs along the same route while entering and leaving port, it was estimated to take a minimum of 250 years to impact 1% of the coral reef along that track. This result suggests that even in the unlikely event that vessels actually transit over coral reefs, the area affected by shredder bags would be very small.

Using location data for actual ship operations and those of known coral reefs, the assessment focused on locations where a vessel could be collocated with known coral reefs within the 1-nmi spatial resolution of the data. This 1-nmi criterion takes into account the potential for lateral transport of the shredder bags or the TDU containers that may move them reef-ward from the discharging vessel. The maximum overlap of vessel and coral reef locations was again observed for the Wider Caribbean Area in vicinity of Puerto Rico and St. Croix. The maximum region of coral reefs impacted was estimated at 0.00005% annually. In other words, it would take a minimum of 2000 years to impact 1% of the coral reef areas of this region. Thus, the potential for exposure based on actual operational data suggests a conclusion similar to that found for the port visit data, that the potential for exposure of coral reefs to surface vessel discharges is insignificant.

The following factors can be used to assess their operations relative to those of surface vessels. Submarines traditionally do not transit in shallow waters and particularly over known coral reefs, except potentially when transiting into and out of port. The conclusion from the surface vessel operations was that solid waste discharges from surface vessels would have an insignificant impact on coral reefs. Submarine solid waste generation rates are significantly less than surface vessels (table 8-2), thus the potential impact from submarine discharges would be significantly less. Restrictions limiting disposal of submarine solid waste to outside of 25 nmi in shallow water areas reduce the likelihood for discharges in coral reef environments. Furthermore, TDU containers sink more quickly through the water column than shredder bags, which reduces their potential lateral transport, i.e., submarines would need to discharge wastes closer to coral reefs than surface ships to impact them. These factors combined with the minimal impact predicted

for surface vessels indicate that the potential impact to coral reefs from submarine TDU waste discharges is insignificant.

**Potential Impacts to Endangered Species.** As part of a fate and effects study of U.S. Navy shipboard solid waste discharges (Chadwick et al., 1996), NRaD examined some of the available information relevant to assessing the potential for impacts to endangered species in MARPOL Special Areas and in the world's oceans. This work was initiated by concerns as to whether burlap bags containing shredded metal and glass discharged from U.S. Navy ships could pose a significant risk to endangered species through ingestion. The qualitative assessment included the following primary objectives relevant to shredded waste discharges: (1) to identify threatened and endangered species found in the world's oceans and specifically those found within MARPOL Special Areas; (2) to identify behavioral patterns inherent for each listed species that would influence their potential to encounter and ingest wastes; (3) to determine the abundance and distribution of proposed solid waste discharges, given historical U.S. Navy operations; and (4) to qualitatively evaluate the potential for impact to threatened and endangered species populations given the estimated likelihood of exposure. In general, quantitative analysis of impacts of solid waste discharges on endangered species is limited by a lack of applicable data.

NRaD's qualitative analysis of the potential for impacts of the surface ship shredder bag waste stream on endangered species (Curtis et al., 1996) concluded that, of the listed species, only gray whales and five species of turtles (green, hawksbill, Kemp's Ridley, loggerhead, and Olive Ridley) were found to have feeding behaviors which could place them at risk for ingestion of bagged waste. For these species it is uncertain whether they would ingest the waste if they encountered it. Although there is no specific evidence for ingestion of this type of waste, the fact that they feed off the sea floor in a relatively non-selective manner indicates that they might inadvertently consume the waste if they came across it.

The likelihood that these species would encounter the waste was, therefore, assessed on the basis of typical feeding behavior, habitat, and diving capabilities of the animals in relation to expected discharge locations, depths, and densities of the waste from the ships. For surface vessels, it is expected that the 12-nmi discharge limit, the extremely low spatial density of shredder burlap bags on the sea floor, the burial of bagged waste by natural sedimentation processes, and the slow deterioration of the waste materials due to corrosion will all serve to minimize the likelihood of exposure to all threatened and endangered species.

For turtles it was found that the limited overlap between feeding areas and discharge areas (coastal vs. >12 nmi offshore), limited diving depths of most species, and the very low spatial density of burlap bags in areas where encounters might possibly occur all combine to reduce the expected exposure to extremely low levels. On this basis, impact to sea turtles due to discharges of bagged solid waste was determined to be very unlikely. Similarly for gray whales it was found that the overlap between the areas and depths where the whales generally feed and significant Navy ship traffic occurs will be very limited. In addition, the filtering mechanism by which gray whales obtain their food generally precludes them from ingestion of large and/or heavy materials. These factors, combined with the general characteristic of extremely low spatial density of bagged waste on the sea floor indicate that the likelihood of impact to gray whales from shredder discharges would be very low. Therefore, neither gray whales nor sea turtles are considered to be at risk from the shipboard shredded material.

The conclusion that shipboard shredded waste has a very low likelihood of impacting endangered or threatened species is the same for the submarine TDU container wastes. The distance from shore restrictions, which are more stringent for submarines, further minimize potential exposures. The relatively large size of the TDU containers suggest that ingestion is not expected to be an important impact to bottom dwellers, especially in the deep sea. The potential for small animals to invade the perforated container and ingest small particles present in the container is real, although the impacts of this are unknown. For bottom-foraging animals such as turtles, the container would probably need to be opened before any of the material could be ingested. However, the very low spatial density and the overlap of regions where turtles forage and TDU containers are allowed to be deposited is limited. This is also true for gray whales.

In summary, there are only a limited number of listed species that display feeding behaviors that could place them at risk for ingestion. For these, the extremely low chance of exposure indicates that the likelihood of impact is very low. Additionally, the continuous rain of sedimentary materials onto the package, particularly in high sedimentation areas, will tend to cover the container and minimize this potential further.

**Time History on the Sea Floor.** Once discharged from a ship, the TDU package is essentially deposited and accumulated on the sea floor forever. Although corrosion and degradation changes its form, the material remains. The primary processes and estimated time scales for the fate of the TDU package are shown schematically in figure 8-6. Once on the bottom, physical and chemical degradation of the materials begins, while natural sedimentation and biological colonization start to cover the container. Further corrosion will result in the potential that the container surface will break open, although this is expected to occur on a time scale of several years. Corrosion, degradation, and fouling continue over the time scales of years to decades to hundreds of years. Depending on the depositional environment, the can is covered in hundreds of years to possibly thousands of years in deep-sea areas having low sedimentation rates. Burial effectively dilutes its biological or chemical impact while covering up the material at the surface. Once buried, continuation of these processes is possible, although probably not important from a biological or geochemical standpoint.

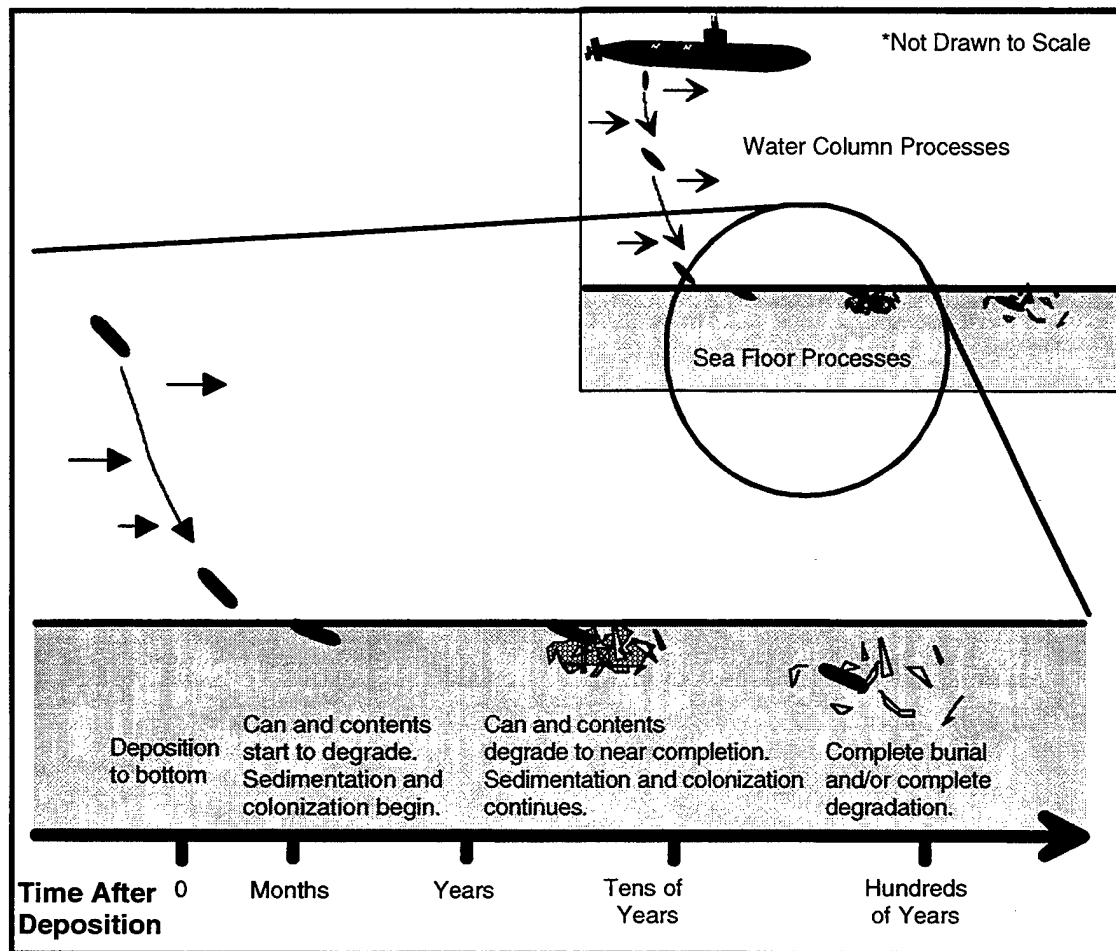


Figure 8-6. Primary processes and expected time scales for the fate of a TDU container in the sea. \*Note, diagram is not drawn to scale; TDU cans are shown relatively larger than actual.

## 8.5 BASIN SCALE ASSESSMENT

This section addresses the impact of solid waste discharges from all submarine operations in each Special Area by comparing them to estimates of other basin-wide inputs. The purpose is to provide a perspective on the relative contribution of ship discharges to the overall loading of Special Areas and to assess the likelihood for either adverse or significant impacts in the overall budgets or processes over basin-wide scales. The basic constituents of the waste stream including organic carbon as cellulose and metals primarily as iron, are already present in most regions from a variety of anthropogenic and natural sources, including river inflow, domestic sewage outfalls, industrial and agricultural discharges, ocean dumping, and natural *in situ* processes such as photosynthesis. While the form of ship generated solid wastes is significantly different from that of these other inputs, the individual constituents can be compared with respect to their overall mass loading. The magnitude of these sources and processes will be addressed, as will consideration of the incremental mass loading from the U.S. Navy surface fleet (Chadwick et al., 1996).

Estimates of mass loading by the submarine fleet in Special Areas are based on waste generation rates and operational profiles. As discussed previously in Section 6.1, the USS *Cincinnati* solid waste generation rate data were used for estimating the paper, cardboard, metal, and glass

components while the generation rate data for oily paper towels come from the NNS (1996) study. These data fixed the mass fraction of the contents of TDU cans as described in table 6-2. Because available operational data provide only a range in the number of operating days for submarines in Special Areas, mass loading estimates are also generated only as a range of values.

The estimated amounts of submarine waste generated annually in Special Areas (see table 8-2) are: 1.4 to 33.3 mt bulk paper/cardboard; 1.6 to 36.1 mt metal, including the containers themselves and weights used for sinking; 0.2 to 5.6 mt glass; and 0.004 to 0.099 mt oily paper towels. The minimum number of cans discharged to produce these annual mass loading estimates ranges from 120 to 2775. These amounts (except for oily paper towels) are compared to the amounts discharged by the U.S. Navy surface fleet (Chadwick et al., 1996) in table 8-2. Annual inputs from the surface fleet range from 235 to 1730 mt for paper/cardboard; 80 to 610 mt metal; and 15 to 112 mt glass. It can be seen that the inputs from the surface fleet are substantially larger than those for the submarine fleet. Typically, the submarine fleet discharges from about 4 to over 50 times less material than the surface fleet. The largest difference in the amount of bulk components discharged by surface ships with that of submarines is for paper/cardboard while the smallest is for metal.

Table 8-2. Annual mass loading estimates of TDU waste components in Special Areas.

Vessel Type	TDU Containers or Shredder Bags	Paper/cardboard (mt)	Total Metal* (mt)	Glass (mt)	Oily Paper Towels (mt)
Submarines	120 - 2775	1.4 - 33.3	1.6 - 36.1	0.2 - 5.6	0.004 - 0.099
Surface Ships	1700 - 179000	16 - 1731	5.8 - 610	1.1 - 112	NA

\* Total Metal includes the metal wastes, container, and steel weights added for ballast.

Waste stream constituents that are of concern from a regional standpoint include those that are either enriched relative to the sediments on which they are deposited, or those that can elicit an adverse response in the environment. Submarine waste stream constituents that are enriched relative to those found in typical sedimentary materials were determined previously to include iron, organic carbon, and tin. From a standpoint of important processes such as eutrophication, oxygen consumption, or toxic biological responses, the constituents of the waste stream that are of concern also include nutrients (nitrogen and phosphorous) and priority pollutants (e.g., zinc).

The total amount of elemental components added to Special Areas by submarines is calculated by multiplying the amount of each bulk material in the waste stream (including the container and ballasting weights) by the abundance of elements making up each component (table 8-1). The result of these calculations are shown in table 8-3. Because the metal portion of the waste stream is about 98%, iron and organic carbon making up about 95% of the paper/cardboard, these two constituents are discharged in nearly the same amounts as their bulk constituents. For both iron and organic carbon, the amounts discharged range from about 1.5 to 35 mt·y<sup>-1</sup>. The amount of Sn discharged annually ranges from 0.01 to 0.16 mt·y<sup>-1</sup>. The amount of nutrients and zinc added to the environment by these discharges can be obtained from the data of Chadwick et al. (1996) and applied to the total waste stream discharges. Nitrogen and phosphorous were found in the paper/cardboard solid phase at concentrations of 410 and 48 mg·kg<sup>-1</sup>, respectively, while zinc was found at a concentration of 6 mg·kg<sup>-1</sup>. Using these values, the mass loading of these constituents range from 0.00001 mt Zn·y<sup>-1</sup> to a maximum of 0.014 mt N·y<sup>-1</sup>.

Table 8-3. Mass loading of iron, organic carbon, tin, nitrogen, phosphorous, and zinc from submarine solid waste discharges.

Element	Annual Discharge (mt)
Fe	1.5 - 35.0
Org C	1.4 - 31.6
Sn	0.01 - 0.16
N	0.0006 - 0.0140
P	0.0001 - 0.0016
Zn	0.0001 - 0.0016

Significant basin-wide sources of the above elemental constituents potentially include rivers, atmospheric fallout, industrial/sewage outfalls, ocean dumping, primary production, and hydrothermal vents. The magnitude of each source type varies with component and with each Special Area. While the primary source of nutrients in the Mediterranean is from rivers, the principal source of zinc is from municipal discharges (UNEP, 1989). In the North Sea, atmospheric input of most metals is thought to be about the same as that for rivers (Hallberg, 1991). However, in all seas the primary source of organic carbon is *in situ* primary production by phytoplankton. Although the form of these inputs are different than that of submarine solid waste, the analysis is designed to provide perspective on the relative elemental loading to Special Areas.

Though most sources have regional impacts, there can be considerable variation on a local scale, particularly in regions close to specific discharges such as those from sewage treatment plants. This, along with patchy *in situ* processes, may lead to somewhat uneven spatial distributions of constituents. On the other hand, the mobile nature of submarines results in discharges that are naturally diffuse and randomly delivered over a wide spatial extent. While local variability can be expected, comparison of magnitudes on a regional scale should remain reasonable.

Data on regional inputs to Special Areas come from a wide range of information available in the literature, much of which is presented in Chadwick et al. (1996). The three regions for which there are the most complete data sets for comparison are the Mediterranean Sea, North Sea, and Baltic Sea. These regions also provide a wide range in the size and type of sources common to Special Areas. While some of the data for these regions could be obtained from tables, much of the data were derived indirectly. For example, Fe and Sn input data were almost non-existent in the literature, and their inputs were derived using riverine-suspended matter loads and their typical crustal abundances of  $48 \text{ mg} \cdot \text{g}^{-1}$  and  $2 \text{ ug} \cdot \text{g}^{-1}$ , respectively (Chester, 1990). As such, the regional input of these metals are probably underestimated. This is probably true for most constituents because all regional sources could not be included in the estimates. Therefore, these data mainly provide context and perspective for submarine solid waste discharges rather than a complete quantification of all sources.

Regional inputs for the elements of concern to the Mediterranean Sea, North Sea, and Baltic Sea are shown in table 8-4. It can be seen from this assessment that by far the major constituent to any of the seas is the *in situ* production of organic carbon. This is followed a distant second by the input of Fe, then by the nutrients and the other two metals. The amount of BOD<sub>5</sub>, associated with the organic particulate matter load of each seas, is also shown in the table. It can be seen from tables 8-3 and 8-4 that individual regional sources are orders of magnitude larger than annual inputs from submarine wastes.

Table 8-4. Annual loading of elements from basin-wide sources to the Baltic Sea, North Sea, and Mediterranean Sea. "Other" refers to other known industrial inputs while blanks indicate no data available.

Special Area Element	Atmosphere (mt.y <sup>-1</sup> )	Rivers (mt.y <sup>-1</sup> )	Municipal (mt.y <sup>-1</sup> )	In Situ (mt.y <sup>-1</sup> )	Other (mt.y <sup>-1</sup> )	Total (mt.y <sup>-1</sup> )
<b>Baltic Sea</b>						
Fe		2.4·10 <sup>5</sup>			2.5·10 <sup>4</sup>	2.7·10 <sup>5</sup>
Org C				7.7·10 <sup>7</sup>		7.7·10 <sup>7</sup>
Sn		1.0·10 <sup>1</sup>			1.0·10 <sup>0</sup>	1.1·10 <sup>1</sup>
N	4.2·10 <sup>5</sup>	4.7·10 <sup>5</sup>	6.0·10 <sup>4</sup>			9.4·10 <sup>5</sup>
P	6.0·10 <sup>3</sup>	3.6·10 <sup>4</sup>	1.2·10 <sup>4</sup>			5.4·10 <sup>4</sup>
Zn	5.0·10 <sup>3</sup>	6.9·10 <sup>3</sup>	4.0·10 <sup>2</sup>			1.2·10 <sup>4</sup>
BOD <sub>5</sub>	3.0·10 <sup>5</sup>	1.2·10 <sup>6</sup>	2.0·10 <sup>5</sup>			1.7·10 <sup>6</sup>

Special Area Element	Atmosphere	Rivers	Municipal	In Situ	Other	Total
<b>North Sea</b>						
Fe		9.6·10 <sup>5</sup>				9.6·10 <sup>5</sup>
Org C				1.8·10 <sup>8</sup>		1.8·10 <sup>8</sup>
Sn		4.0·10 <sup>1</sup>				4.0·10 <sup>1</sup>
N	2.4·10 <sup>5</sup>	7.4·10 <sup>5</sup>			9.5·10 <sup>4</sup>	8.4·10 <sup>5</sup>
P		5.3·10 <sup>4</sup>			2.5·10 <sup>3</sup>	5.5·10 <sup>4</sup>
Zn	9.3·10 <sup>2</sup>	4.2·10 <sup>3</sup>			9.9·10 <sup>3</sup>	1.5·10 <sup>4</sup>
BOD <sub>5</sub>						1.3·10 <sup>6</sup>

Special Area Element	Atmosphere	Rivers	Municipal	In Situ	Other	Total
<b>Mediterranean Sea</b>						
Fe		1.7·10 <sup>7</sup>				1.7·10 <sup>7</sup>
Org C				1.3·10 <sup>8</sup>		1.3·10 <sup>8</sup>
Sn		7.0·10 <sup>2</sup>				7.0·10 <sup>2</sup>
N		8.0·10 <sup>5</sup>	2.0·10 <sup>5</sup>			1.0·10 <sup>6</sup>
P		3.0·10 <sup>5</sup>	5.7·10 <sup>4</sup>			3.6·10 <sup>5</sup>
Zn		6.9·10 <sup>3</sup>	1.8·10 <sup>4</sup>			2.5·10 <sup>4</sup>
BOD <sub>5</sub>		1.8·10 <sup>6</sup>	1.5·10 <sup>6</sup>			3.3·10 <sup>6</sup>

A comparison of the maximum annual inputs of submarine TDU wastes to the minimum total inputs from known regional sources indicates that submarine wastes are an insignificant fraction of the basin-wide loading. This comparison, summarized in table 8-5, is conservative, given that the maximum TDU waste loading is compared to minimum regional sources. The annual input of submarine waste materials ranges from 0.0000008% to 0.013% of regional sources, except for Sn which reaches a relative level of 1.4%. Considering Sn to be the worst case relative loading, submarines would need to discharge for 70 years to discharge an equivalent amount of Sn derived from one year of regional inputs. For phosphorous, the number of equivalent years of submarine discharge is 60 million years.



The fact that submarine discharges are a tiny fraction of other regional inputs suggests that from a basin-wide perspective, the added amounts of N and P will have an insignificant impact on the nutrient chemistry or budgets of any sea and, hence, will be unimportant from a eutrophication standpoint. The added amount of organic carbon is also too small to have any impact from a basin-wide perspective, thus, the added amount of oxygen demand on each sea will be insignificant. This can also be seen from the relative BOD<sub>5</sub> numbers shown in table 8-4, which are derived from the BOD<sub>5</sub> of pulped paper measured in Chadwick et al. (1996). The added amounts of Fe, Sn, and Zn by submarine discharges are also too small to be of consequence to the metal chemistry of these seas. Of all constituents, the added amount of Sn from TDU cans is potentially the highest relative source and it is a small fraction of basin-wide sources.

Table 8-5. Comparison of maximum annual TDU waste inputs to Special Areas with estimates of the minimum annual regional loading. Equivalent years refers to the number of years of submarine discharges required to equal one year of regional discharges.

	Maximum TDU Input (mt.y <sup>-1</sup> )	Minimum Regional Input (mt.y <sup>-1</sup> )	TDU <sub>Max</sub> /Basin <sub>Min</sub>	Equivalent Years
Fe	35.0	270,000	0.013%	7.7·10 <sup>4</sup>
Org C	31.6	77,000,000	0.00004%	2.4·10 <sup>6</sup>
Sn	0.16	11	1.4%	7.0·10 <sup>1</sup>
N	0.014	840,000	0.000002%	4.2·10 <sup>3</sup>
P	0.002	36,000	0.0000008%	6.0·10 <sup>7</sup>
Zn	0.002	12,000	0.00002%	6.0·10 <sup>6</sup>
BOD <sub>5</sub>	2.3	1,300,000	0.0002%	5.6·10 <sup>5</sup>

The added amount of oxygen consumed from corrosion of TDU containers can be estimated using the corrosion rate, stoichiometry, and abundance of Fe in the can. As discussed in Chadwick et al. (1996), the corrosion of Fe results in 0.75 moles of oxygen used for each mole of Fe oxidized. This stoichiometry leads to roughly 170 moles of O<sub>2</sub> utilized for complete corrosion of a TDU can and its contents. Given an annual discharge that ranges between 120 and 2775 TDU cans, the total amount of oxygen utilized during corrosion, if complete oxidation occurred in one year, would be between 0.65 to 15.1 kg of oxygen. Standing stocks of dissolved oxygen in Special Areas range in the trillions of kg and, hence, the consumption of oxygen from the corrosion process is an insignificant factor on the overall oxygen budget of Special Areas. Given that the corrosion process takes longer than a year further reduces this burden on oxygen.

It should be noted that the long-term placement of TDU containers on the bottom of San Diego Bay resulted in some hydrogen sulfide production within the can as determined by smell. Although there may be a localized reduction in oxygen within the cans from chemical or biochemical processes, this will not cause an impact on a regional basis.

Assessing potential effects at the sea floor on a basin-wide basis also requires consideration of how much of the sea floor area is likely to be impacted. This can be addressed by looking at the amount of sea floor covered by TDU cans either on a percentage basis or by assessing their sea floor density. The amount of surface area covered can be obtained using the number of cans

discharged annually (using the  $7 \text{ d}^{-1}$  discharge rate as discussed in Section 6.1) along with their frontal surface area ( $1400 \text{ cm}^2$ ) and comparing this to the sea floor surface area in Special Areas. The amount of surface area covered annually by TDU cans is estimated to range from  $40 \text{ m}^2$  to  $910 \text{ m}^2$ . The surface area of Special Areas (excluding the Antarctic region) ranges from  $2.4 \cdot 10^{11} \text{ m}^2$  in the Gulfs Area up to a maximum of  $4.2 \cdot 10^{12} \text{ m}^2$  in the Wider Caribbean Region. Using the maximum annual input of containers and the range of sea floor surface area represented by the above two Special Areas, the percentage of surface area covered annually by TDU cans ranges from 0.00000002 to 0.0000004%. The density of containers, therefore, ranges from 1 can per  $650 \text{ km}^2$  up to 1 can per  $40 \text{ km}^2$ . The maximum density of 1 can per  $40 \text{ km}^2$  is roughly equivalent to one can in a region that is nearly 3.5 nmi on a side. The results discussed here are summarized in table 8-6.

Because the TDU coverage is based on an annual discharge, and the input rate is much faster than the degradation, corrosion, and burial rates, the percent coverage or density of cans should be considered over time. Based on the annual input, it would take between roughly 2.6 and 46 million years to cover just 1% of the sea floor of Special Areas with submarine solid waste discharges. It would take between 40 and 650 years of discharges to reach a density of one TDU can  $\cdot \text{km}^2$  if this was used as the benchmark. The calculation of these times do not take into account the slow "disappearance" of the material from the processes of degradation, corrosion, and burial. Although from an elemental standpoint these materials do not ever disappear, from an aesthetic or litter standpoint, the material does indeed "disappear" as a function of time, and in this way, the times calculated above can be considered to be minimums.

The incremental amount of sea floor covered by submarine discharges with that of U.S. Navy surface vessel discharges can be estimated in similar fashion to the above. Using a frontal surface area of shredder bags of  $2000 \text{ cm}^2$  and the estimated annual discharge rates for the two seas above gives a range of sea floor coverage between  $14,400 \text{ m}^2$  for the Gulfs Area and  $26,600 \text{ m}^2$  in the Wider Caribbean Region (table 8-6). The percentage of sea floor covered by bags, thus, ranges from 0.0000006 to 0.000006%. The additional amount of sea floor covered by submarine discharges using the maximum annual discharges translates into 6% for the Gulfs Area and 3% for the Wider Caribbean Region. Considering it will take between roughly 160,000 to 1.5 million years to cover just 1% of the sea floors of these Special Areas with surface vessel discharges, the additional amount introduced by submarines is inconsequential.

As discussed previously, the discharge density of submarine wastes for Special Areas is greater than that estimated for the open ocean. Thus, estimates of sea floor coverage discussed above for Special Areas are therefore higher than those expected for open ocean areas. Given that the sea floor coverage of Special Areas is already insignificant suggests that the same is true of sea floor coverage expected in the open ocean.

Table 8-6. Annual sea floor coverage of submarine TDU cans and surface vessel shredder bags relative to total sea floor area available in the Gulfs Area and Wider Caribbean, assuming no degradation of the contents.

<b>Submarine Fleet</b>	<b>Gulfs Area</b>	<b>Wider Caribbean Region</b>
Sea Floor Surface Area (m <sup>2</sup> )	2.39·10 <sup>11</sup>	4.24·10 <sup>12</sup>
Maximum Surface Area of TDU Cans Discharged Annually (m <sup>2</sup> )	910	910
Maximum Sea Floor Coverage of TDU Cans Annually (%)	0.0000004	0.00000002
Maximum Sea Floor Coverage of TDU Cans Annually (km <sup>2</sup> ·TDU Can <sup>-1</sup> )	40	650
Minimum Years to cover 1% of Sea Floor (Y)	2.6·10 <sup>6</sup>	4.6·10 <sup>7</sup>
<b>Surface Fleet</b>		
Surface Area of Bags Discharged Annually (m <sup>2</sup> )	14400	26600
Annual Sea Floor Coverage of Shredder Bags and Cans(%)	0.000006	0.0000006
Incremental Coverage Added by Submarine Fleet (%)	6%	3%

## 9.0 CONCLUSIONS

This section summarizes findings and conclusions regarding the environmental fate and effects of the TDU waste stream in MARPOL Special Areas. The findings are based on an assessment of the discharge conditions, waste stream characteristics, water column and sea floor processes on both local and basin-wide scales. The findings of this study indicate that the discharged TDU containers as proposed will have no significant environmental consequences on a local or basin-wide scale in Special Areas. Given the fact that oceanographic conditions of Special Areas span those found in the open ocean and that the density of submarine discharges in the open ocean is less than that of Special Areas, indicates that there will also be no significant environmental consequences of these discharges in the open ocean.

**Discharge Conditions.** A TDU container with its contents of compressed paper, metal, glass, oily paper towels, and steel weights is discharged as a single unit. The amount of solid waste generated by a crew complement of 130 requires the discharge of a minimum of three TDU cans daily. Though multiple containers can be discharged simultaneously, it is unlikely that the containers will be deposited next to each other on the sea floor. Hence, the amount of sea floor impacted from a single discharge event can be estimated to be equivalent to the dimension of a single container. Current operational requirements imposed by OPNAVINST 5090.1B that restrict discharges from submarines to greater than 12 nmi from shore in water depths exceeding 1829 m or at greater than 25 nmi from shore in all water depths serve to minimize the areal extent for potential impacts of waste discharges. They also serve to minimize the likelihood of impacting sensitive biological endpoints that tend to reside in shallow-water environments.

**Waste Stream Characteristics.** The principal components of the waste stream considered are paper and cardboard (43%), metal contents (21%), ballasting weights (18%), glass (7%), the TDU container itself (7%), and oily paper towels (4%). The waste stream totaling about 28 kg is packed into a volume of about 25 L with a footprint of 1400 cm<sup>2</sup>. This discrete package provides a waste stream mix composed of organic and inorganic material in roughly equal proportions. The organic material is composed mostly of organic carbon in the form of cellulose, while the inorganic material is made up of the metal components primarily in the form of iron.

An average settling rate of a TDU can was measured at 133 m·min<sup>-1</sup> indicating that settling times would range from seconds to minutes in most Special Areas. This suggests that the cans will have minimal impact in the water column and that they are unlikely to travel far from their discharge point. However, the relatively high sinking speed is unlikely to result in breakage of the container upon impact with the sea floor as determined from field measurements.

Chemical analyses of the container and its contents indicate that the waste stream package is enriched in iron, organic carbon, and tin relative to the sedimentary material upon which it will ultimately be deposited. The only priority pollutant consistently found in seawater leachates of the waste materials was zinc, but this was observed at levels below concentrations that might pose a threat to the environment. Other contaminants measured in individual samples included copper, phthalate esters, and phenol. The observed levels of phthalates would be diluted by surrounding seawater to levels below those of potential concern within approximately 15 cm of the container, using conservative estimates of dilution. It is estimated that even the anomalous copper contaminant would be diluted to levels below those considered to be of ecological concern within 70 cm of the container.

Biological effects were tested using standardized bioassays on seawater leachates of the TDU and its contents. The most sensitive endpoints indicated that a leachate concentration of about 4% caused an inhibition of growth or light production, and measures of stress on two phytoplankton species, regardless of whether or not oily paper towels were present. An estimated no-effects concentration of 0.4% would be predicted to occur within 122 cm of the container surface from dilution with surrounding seawater.

Biological effects were also tested using TDU cans that were placed on the bottom of San Diego Bay. Standard bioassays were run on seawater samples collected from within and from 50 cm away from two TDU cans. No effects were observed for the most sensitive test species at 50 cm away, and a no-effects concentration was predicted to occur at only 15 cm away. While toxic effects could be elicited in some sensitive test organisms, TDU cans placed in San Diego Bay for several months were colonized by a number of indigenous species, suggesting that the containers and associated wastes are not necessarily harmful to all biological activity.

**Water Column Processes, Fate, and Effects.** The rapid sinking of the TDU containers, once discharged into the ocean, minimizes the likelihood for any effects in the water column. Lateral transport of a container under typical on-shore flow and bottom slope conditions is minimal with the implication that the waste stream will not travel far from its discharge point. When discharged beyond either the 12- or 25-nmi limit with water depth conditions, the TDU containers will not be a source of coastal litter.

**Sea Floor Processes, Fate, and Effects.** The ultimate fate of the TDU waste stream is deposition, degradation, corrosion, and burial on the sea floor. Thus, the materials or their by-products of corrosion and degradation will remain forever within the sedimentary record. The relative importance of these processes is ultimately controlled by the conditions of the depositional environment, which for MARPOL Special Areas, covers the full spectrum of those found anywhere in the world's oceans. However, because of discharge restrictions, the packages are more likely to find their way into deep-water environments rather than shallow-water areas which tend to have more sensitive biological endpoints.

Because of the discrete nature and random distribution of the discharges, the processes and effects of concern are those of a single TDU container with its contents on the sea floor. Other than enrichments of organic carbon, iron, and tin, the waste package is composed of materials that are not dramatically different from those occurring naturally on the sea floor. Complete degradation of the organic materials and corrosion of the inorganic components will occur over a time frame of years to decades or possibly hundreds of years, depending on the nature of the depositional environment. Competing with this process is natural sedimentation that eventually will result in complete burial. The time frame for this is also dependent on the depositional environment, but is likely to span hundreds to thousands of years in the deep sea. The balance of these rates will play an important role in how much and what form the material is incorporated into the sedimentary record.

Possible adverse effects of a single TDU container and its contents on the sea floor include toxicological effects, physical damage, and effects from ingestion. While TDU cans may contain materials that can elicit a toxic response in some test organisms under laboratory conditions, the effects were considered within the context of real-world conditions. When the most sensitive biological toxic response to a seawater solution of the TDU container was considered, dilution to a no-effects concentration was predicted to occur within 122 cm of the container. Based on *in*

*situ* measurements, however, a no-effects concentration was predicted to be reached at 13 cm from a container. The implication is that long-term exposure on the sea floor may cause some toxic effects to some sensitive organisms that are in very close proximity to the container. However, biofouling of the cans in San Diego Bay qualitatively suggests that many organisms can thrive within the cans themselves.

Some physical damage to the benthos may occur upon the container's initial impact with the bottom or if it is moved around under anomalously high-current conditions. The potential for damage to particularly sensitive benthic species such as coral reefs was therefore addressed. It was determined from a review of ship operations and the distribution of coral reefs in Special Areas that the likelihood that submarine discharges would impact coral reefs is insignificant.

Threatened or endangered species were considered the sensitive biological endpoints from the standpoint of potential effects from ingestion. A review of the distribution of threatened and endangered species in MARPOL Special Areas, their feeding behaviors, and the likelihood of collocation with submarine discharges indicated that there is an exceptionally low probability for effects from ingestion.

**Basin Scale Assessment.** Solid waste mass loading from submarine operations on a basin-wide scale was assessed in this study with the goal of providing perspective on the relative contribution of ship discharges and their potential for impacts in Special Areas. The maximum annual input of paper/cardboard, metal, glass, and oily paper towel components to Special Areas is estimated at 33, 36, 6, and 0.1 mt, respectively. These materials supply a minuscule amount of the organic carbon, iron, tin, nutrients or contaminants relative to those derived from other regional inputs such as rivers and industrial discharges. The basin-wide impact on sea floor processes such as oxygen depletion or eutrophication is, thus, inconsequential. From a perspective of sea floor coverage, the amount of surface area covered annually by TDU cans ranges up to a maximum of 0.0000004% for Special Areas. At the maximum annual rate input rate it would take at least 2.5 million years to cover just 1% of the sea floor of Special Areas with submarine solid waste discharges. From a basin-wide perspective, the discharge of the submarine solid waste in Special Areas should have no adverse environmental impact.

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## **Appendix A**

### **BIOLOGICAL TEST AND CHEMICAL ANALYSES**

Source: MEC Analytical  
2433 Impala Drive  
Carlsbad, California

# **ELUTRIATE TOXICITY TESTING OF TRASH DISPOSAL UNITS**

**PREPARED FOR**

**NAVAL COMMAND, CONTROL  
AND  
OCEAN SURVEILLANCE CENTER  
(NCCOSC)  
RDT&E DIVISION**

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## 1.0 INTRODUCTION

The Naval Command, Control and Ocean Surveillance Center (NCCOSC), RDT&E Division, San Diego, California is conducting research on potential toxicity to the marine, planktonic, pelagic and benthic communities from United States Navy submarine Trash Disposal Units (TDU). The work described here consists of chemical analyses and toxicity testing on elutriates prepared from four TDUs.

The U.S. Environmental Protection Agency (EPA) and the U.S. Army Corps of Engineers (ACOE) have established marine organism bioassays as the primary means for assessing the environmental risks associated with the discharge of solid materials into territorial waters. To examine the potential impacts on marine organisms from the discharge of the TDU, elutriate toxicity tests were conducted by MEC Analytical Systems, Inc. (MEC) in Carlsbad, California. Acute and chronic toxicity tests were performed on four organisms using elutriates derived from the four TDUs. Testing was initiated on November 5 and completed on November 13, 1996. Microtox analysis was conducted by Azur Environmental (formally Microbics Corporation), in Carlsbad, California. Chemical analyses of elutriates were performed by Columbia Analytical Services (CAS) laboratories in Kelso, Washington.



## 2.0 METHODS

All methods and procedures employed in this program, with the exception of Microtox, followed guidelines established by the EPA and the USACOE in "General Requirements for Sediment Testing of Dredged Material Proposed for Ocean Disposal" (EPA/USACOE 1991). This document is commonly identified as the "Green Book". Methods and procedures for Microtox follow the guidelines established by Azur Environmental.

### 2.1 Custody of Samples

Four TDU samples (TDU 1 through TDU 4) were received by MEC on November 1, 1996. Upon receipt of the TDUs, each container was processed by MEC personnel following established chain of custody procedures, assigned a unique test number, packaged in clean food grade plastic bags and placed into a refrigerated room maintained at 4 C, until testing. Sample receipt observations indicated that the contents of each TDU were tightly compacted and completely closed.

The contents of the TDU's are listed below:

<b>TDU I.D.</b>	<b>Weight (lbs)</b>	<b>Contents (%)</b>
TDU-1	40.0	2 weights, paper, metal, rags
TDU-2	45.0	1 weight, newspaper, aluminum, metal, glass
TDU-3	48.0	1 weight, glass, paper, food, plastic, textiles
TDU-4	52.0	2 weights, photos, paper, glass, oily rags, cans

### 2.2 Test Water Collection

The Green Book specifies that seawater used in all aspects of the bioassay testing should be obtained from the proposed dump site. Since large volumes of water are necessary to perform the required tests, the ACOE has allowed water from alternative sites to be used. All water used in this program was collected from Scripps Institution of Oceanography, La Jolla, California.

### 2.3 Elutriate Preparation

Four TDU elutriate preparations were examined following Green Book guidelines, a 20% (4:1 seawater to sample) elutriate was prepared on November 4, 1996. Seawater/TDU proportioning was based on weight rather than volume. Due to the physical nature of the units and the desire to test each unit intact and unopened, it was not possible to mechanically stir the sample. Instead, each TDU was manually agitated for 30 minutes using clean PVC pipe.

After the mixing phase, elutriates were allowed to settle for one hour. Samples were then decanted into clean, five gallon polyethylene containers. Elutriates were held in the dark at 4 C for less than twenty-four hours prior to the initiation of testing. Additional samples were collected into clean 1 gallon containers, and archived.

## 2.4 Organism Collection and Handling

Four test organisms were used in this study: mysid shrimp, *Mysidopsis bahia*; inland silverside, *Menidia beryllina*; diatom, *Skeletonema costatum*; and a marine fluorescent bacteria, *Photobacterium phosphoreum*.

Mysids and *M. beryllina* were provided by Aquatic Indicators in St. Augustine, Florida and were received the day of the test. Upon receipt, the test animals were fed freshly hatched *Artemia* nauplii (brine shrimp) and acclimated to test conditions for approximately 6 hours prior to test initiation.

*S. costatum* cultures were provided by the University of Texas at Austin. *S. costatum* were received in concentrated culture and inoculated into test chambers directly from the culture vial. Bacteria for Microtox testing was supplied by Azur Environmental.

## 2.5 Analytical Chemical and Bioassay Methods

Tests protocols followed those described in the EPA/ACOE Green Book, and were supported by ASTM and/or EPA protocols. With the exception of Microtox, testing was performed as a standard, five concentration dilution series. The bacterial bioluminescence test (BBT) is a metabolic inhibition test that uses a suspension of luminescent bacteria as test organisms (ASTM 8050). For the acute *Photobacterium phosphoreum* test, light produced by test organisms was measured under standard conditions. The bacteria were then exposed to a variety of sample concentrations for five and fifteen minute intervals, and their light output was measured a second time. Reduction in light output between the first and second measurements is directly proportional to the toxicity of the test sample. Concentrations tested were 0, 18.2, 27.3, 36.4, 45.5, 54.6, 63.9, 72.8, and 81.9 percent elutriate. After exposure of the sample, data reduction methods were applied and a dose-response curve was produced. This curve allowed the identification of an "effective concentration" (EC<sub>50</sub>) where light output was reduced by fifty percent.

Eight day old mysids and the *M. beryllina* were used in the chronic, seven day exposure studies. The concentrations used for the mysid, *M. beryllina*, and algae, *S. costatum* tests were 0, 6.25, 12.5, 25, 50, and 100 percent elutriate. Each concentration for the mysid test had eight replicates, with five animals per replicate, resulting in a total of 40 animals per test concentration. The *M. beryllina* test included four replicates, per concentration with 10 fish per replicate, resulting in a total of 40 animals per test concentration. Final test volumes for both tests was 250 milliliters. Test substances and controls were renewed daily. Biological observations made were survival, which was determined daily and at the end of the testing period, and growth after seven days. Criteria for death was defined as lack of movement of an organism when a pulse of water was applied to an individual organism. To determine the increase in weight (growth), animals were dried overnight and weighed in a pre-tared "weigh

boat". The growth (weight) was determined by subtracting the tare weight (weigh boat only) from the final weight (weigh boat and surviving animals). Test results were based on the survival and growth of the organisms as compared to the controls. Quality Control passing criteria for the *M. beryllina* and mysid was established at greater than 80 percent of control test organisms surviving. Passing criteria for growth was an average dry weight in the control of greater than 0.43 milligrams (mg) for the fish larvae, and greater than 0.20 mg for the mysids. Reference toxicity tests were performed on each test species.

The *S. costatum* test consisted of three replicates for each test concentration with approximately 10,000 cells/ml initially inoculated into each test chamber. The test is designed to determine the effect of test solutions on the growth of marine algal (diatoms) during a 96 hour testing period. Initial algal inoculant concentrations were determined by microscopic examinations of cells on a counting chamber (hemacytometer). A verification count was performed to validate the accuracy of the inoculation. Test chambers used were clean, 125 milliliter Erlenmeyer flasks with an exposure volume of 100 milliliters. Dilution water was ("f/2") alga media prepared under ASTM 1992 guidelines. Test chambers were held in a photoperiod of 14 hours light:10 hours dark. Quality control criteria (ASTM 1992) was established as a final average density of 100,000 cells per milliliter in controls. Final growth counts were measured as an average of two counts from each treatment. Reference toxicity tests were performed.

Test material was collected for chemical analysis (EPA Priority Pollutant 126) within twenty-four hours of elutriate preparation. The table below presents a methods list of analytes examined by EPA method number. Detection limits are presented with chemistry results in Appendix A.

ANALYTE	EPA METHOD(s)
Total Metals	6010A/7060/7421/7841/7470
Cyanide	335.2
Phenolics	420.1
Organochlorine Pesticides	3520B
Aroclor Polychlorinated Biphenyls	608
Volatile Organic Compounds	624

## 2.6 Statistical Analysis

Toxicity test results were analyzed with the statistical package ToxCalc 5.0 (Tidepool Scientific Software). ToxCalc is a comprehensive statistical application designed for analyzing and reporting dose-response data generated from toxicity testing. ToxCalc evaluates toxicity indices using U.S. EPA approved parametric and non-parametric statistical methods. All statistical analyses reported follow standard guidelines for acute and chronic toxicity data analysis.

ToxCalc categorizes the main statistical approaches into two main groups. Hypothesis based tests yield a No Observed Effect Concentration (NOEC) and a Lowest Observed Effect Concentration (LOEC). Statistical options used for parametric hypothesis tests include the Dunnett's Multiple Comparison Test, intended for comparing multiple treatments with a single control; Bonferroni Adjusted t-Test, used when the data set was unbalanced; Homoscedastic t-Test, conducted as a one-tail test, intended for comparing a single treatment with a single control or when unequal variance was detected by the F-Test; and the Fisher's Exact test, employed when the treatments are replicated, but there are only two possible outcomes per replicate (e.g., alive or dead).

The Bartlett's Homogeneity Test was used to determine equal variance across all treatments and control. Non-parametric hypothesis tests used to analyze data included Steel's Many-One Rank Test, used for comparing multiple treatments with a single control, was used when the normality assumption was not met; and Wilcoxon Rank Sum Test, intended as a less powerful test, was used when the data set was unbalanced.

The point estimate approach was used to determine a concentration that would cause a predetermined level of effect (e.g., 50 percent mortality, LC<sub>50</sub>). Point estimate procedures applied included a Maximum Likelihood Regression method, suitable only when data conforms to the model, this method can derive multiple endpoints and produce 95 percent fiducial limits of the selected endpoints; Spearman-Kärber Method used to estimate the median lethal concentration (e.g., LC<sub>50</sub>), or the median effective concentration (e.g., EC<sub>50</sub>); and Linear Interpolation (ICp) method used to calculate point estimates for continuous data (e.g., growth).

### **General Terms used in the summary report are listed below:**

#### **Hypothesis Testing Results:**

- NOEC** No Observed Effect Concentration. The highest concentration tested causing no statistically measurable effect to the test system compared to the control organisms.
- LOEC** Lowest Observed Effect Concentration. The lowest concentration tested causing a statistically measurable effect to the test system compared to the control organisms.

#### **Point Estimate Techniques:**

- LC<sub>50</sub>** Median Lethal Concentration. The concentration of test substance required to kill 50 percent of the test organisms during the testing period.
- IC<sub>50</sub>** Inhibition Concentration. The concentration of test substance that produces a change in a measured variable (e.g., growth) during the testing period.
- EC<sub>50</sub>** Effective Concentration. The concentration of test substance that has an effect on 50 percent of the test organisms during the testing period.

### 3.0 RESULTS AND DISCUSSION

#### 3.1 Chemical Analyses

Chemical analysis (EPA Priority Pollutants 126) was performed on elutriates generated from each TDU. Reporting limits were within QA/QC acceptance limits with the exception of one of the surrogate recoveries for Semivolatiles in TDU-3, and the method blank. Both recoveries were above normal laboratory control limits. The error associated with elevated recoveries equates to a high bias. Greater than normal surrogate recoveries indicate a higher than normal chemical extraction efficiency. Since none of the target analytes were detected in TDU-3, elevated recoveries have no significant influence on the reported results.

Volatile organics, semi-volatile organics, organochlorine pesticides, inorganic parameters, and polychlorinated biphenyls were not detected in any of the elutriate solutions with the exception of TDU-3 where total phenolics (0.05 ppm) and Phenol (34 ppb) were detected.

Metals concentrations in elutriate solutions were very low. Of the metals examined, zinc was found to be elevated in all four samples. Results are as follows: TDU-1, 23 ppb; TDU-2, 21 ppb; TDU-3, 23 ppb; and TDU-4, 21 ppb. Copper was found only in TDU-1 (191 ppb). Complete chemistry data is presented in Appendix A.

#### 3.2 Biological Analyses

Acute and chronic toxicity tests were performed on four test species. Bioassay results are summarized in Tables 1 through 4. Analytical reports specific to each type of test and laboratory raw data are provided as Appendix B.

With the exception of the Microtox test, all bioassay endpoints were significantly different from comparable controls. The Microtox test system presents toxicity results in the form of general toxicity rankings and EC<sub>50</sub> values. TDUs 1, 2, 3, and 4 had EC<sub>50</sub> predicted values in excess of the highest concentration tested (81.9% elutriate), and ranking levels were defined as "slightly toxic" or "non-toxic". TDUs 1, 2 and 3 had a ranking level of slightly toxic, but the predicted EC<sub>50</sub> value for each was greater than the highest concentration tested. TDU-4 had a predicted EC<sub>50</sub> value of greater than 100 percent elutriate and a ranking level of non-toxic.

The *S. costatum* growth test was the most sensitive indicator of toxicity. IC<sub>50</sub> values for all TDUs ranged from 3.65 percent (TDU-3) to 10.77 percent (TDU-1). TDU-1 was the only unit tested that generated a NOEC of equal to, or greater than, the lowest test concentration examined (6.25 percent elutriate). Substantial bacterial growth was noted in all concentrations tested, with the exception of the controls, during the daily observations. Upon termination of the test, large numbers of small, ciliated cells were observed clustering around living *S. costatum* cells. Test dilution water and elutriate used in the algal growth test was filtered to 0.45  $\mu$ m prior to initiation of testing to remove potential algal contaminants. Since there was no indication of bacterial growth in the control replicate, TDU elutriates are assumed to be the source of the observed bacteria. It is possible that the toxic effects observed are the result of direct actions of the bacteria (pathogen) or by competing for nutrients in the test media. This issue could be addressed by performing a second test examining the effects of sterile, filtered elutriates.

Survival for the *M. beryllina* test in 100 percent elutriate range from 17.5 percent (TDU-4) to 50.0 percent (TDU-3). Survival in 100 percent elutriate for TDU-3 was 50.0 percent and the LC<sub>50</sub> value was estimated to be greater than 100 percent due the variable nature of the data. TDU-4 survival (100 percent elutriate) was 17.5 percent and the LC<sub>50</sub> was 73.4 percent elutriate. Test chambers were aerated after twenty-four hours of exposure due to a dramatic drop in dissolved oxygen (D.O.). The drop in D.O. may be the result of bacterial growth observed in the *S. costatum* test. It is not known if the decrease in available oxygen was responsible for the observed mortality, however, this possibility exists. IC<sub>50</sub> values for growth were greater than 100 percent elutriate for all samples, indicating that TDU elutriates had no effect on the growth endpoint.

Mysid survival in 100 percent elutriate from TDU-1 was 5 percent at the end of the seven day testing period, with the LC<sub>50</sub> value estimated to be 53.1 percent. Copper was present at 191 ppb in TDU-1 and was below the detection limit for TDU-2, 3, and 4. Results from reference toxicant testing, using copper sulfate as the toxicant, provided an LC<sub>50</sub> value of 58.7 ppb. It is possible that the toxic effect observed from TDU-1 is the result of high copper found in the elutriate. Other survival results range from 42.5 (TDU-2) to 70 percent (TDU-3). Variability between replicates, within doses, for all four elutriates was demonstrated. LC<sub>50</sub> values were generated by comparing the controls to 100 percent leachate using the linear interpolation technique. This analysis, was chosen due to the variable nature of the data, and the fact that there was less survival at lower concentrations than at higher concentrations. Like the *M. beryllina* growth data, the IC<sub>50</sub> for mysid growth was greater than 100 percent elutriate indicating that TDU elutriates have no effect on the growth endpoint.

### Toxicity Statement

The potential for toxic effects to marine water column dwelling organisms, as a result of the discharge of TDUs, was examined. Of the four species tested, only the algae, *S. costatum*, had a 50 percent effect that was lower than a 50 percent TDU elutriate concentration. If the TDUs were subject to general Federal ocean dumping guidelines for dredge materials, all four units tested would passed the liquid suspended particulate phase discharge model. This model considers the "LC<sub>50</sub>," the amount of material dumped, the method of dumping and the potential for dispersion of the solid material, and was designed to protect water column species.

If the elutriate generated by the TDUs were considered effluent and regulated under Federal NPDES guidelines, the NOEC and the concentration at boundary of the zone of initial dilution (ZID) would be considered in the determination of a significant toxic effect. The ZID boundary is most often defined as a distance from the effluent source that is equal to the depth of the water into which the effluent is discharged. Given the conservative nature of the NPDES costal discharge regulations, the toxicity results of this study and the volume of "effluent" expected to be evolving from a TDU, no toxicity should be expected if the TDUs are dumped into open waters greater than one meter in depth.

**TABLE 1****Summary of Test Results For TDU-1**

Test Type	Survival (100% Elutriate)	LOEC	NOEC	Point Estimate Result
<i>Mysidopsis bahia</i> (Survival)	5%	100%	50%	IC <sub>50</sub> : 53.13%
<i>Mysidopsis bahia</i> (Growth)		50%	25%	IC <sub>50</sub> : >100%
<i>Menidia beryllina</i> (Survival)	32.5%	12.5%	6.25%	EC <sub>50</sub> : 56.62%
<i>Menidia beryllina</i> (Growth)		>100%	100%	IC <sub>50</sub> : >100%
<i>Skeletonema</i> (Growth)		12.5%	6.25%	IC <sub>50</sub> : 10.77%
Microtox (15 Min.)				EC <sub>50</sub> : 90.2%

**TABLE 2**  
**Summary of Test Results For TDU-2**

Test Type	Survival (100% Elutriate)	LOEC	NOEC	Point Estimate Result
<i>Mysidopsis bahia</i> (Survival)	42.5%	6.25%	<6.25%	IC <sub>50</sub> : >100%
<i>Mysidopsis bahia</i> (Growth)		>100%	100%	IC <sub>50</sub> : >100%
<i>Menidia beryllina</i> (Survival)	57.5%	100%	50%	EC <sub>50</sub> : >100%
<i>Menidia beryllina</i> (Growth)		>100%	100%	IC <sub>50</sub> : >100%
<i>Skeletonema</i> (Growth)		6.25%	<6.25%	IC <sub>50</sub> : 3.86%
Microtox (15 Min.)				EC <sub>50</sub> : 81.9%



**TABLE 3****Summary of Test Results For TDU-3**

Test Type	Survival (100% Elutriate)	LOEC	NOEC	Point Estimate Result
<i>Mysidopsis bahia</i> (Survival)	70%	6.25%	<6.25%	IC <sub>50</sub> : >100%
<i>Mysidopsis bahia</i> (Growth)		100%	100%	IC <sub>50</sub> : >100%
<i>Menidia beryllina</i> (Survival)	50%	6.25%	<6.25%	EC <sub>50</sub> : >100%
<i>Menidia beryllina</i> (Growth)		>100%	100%	IC <sub>50</sub> : >100%
<i>Skeletonema</i> (Growth)		6.25%	<6.25%	IC <sub>50</sub> : 3.65%
Microtox (15 Min.)				EC <sub>50</sub> : >81.9%

**TABLE 4**  
**Summary of Test Results For TDU-4**

<b>Test Type</b>	<b>Survival (100% Elutriate)</b>	<b>LOEC</b>	<b>NOEC</b>	<b>Point Estimate Result</b>
<i>Mysidopsis bahia</i> (Survival)	50%	100%	50%	IC <sub>50</sub> : >100%
<i>Mysidopsis bahia</i> (Growth)		>100%	100%	IC <sub>50</sub> : >100%
<i>Menidia beryllina</i> (Survival)	17.5%	100%	50%	EC <sub>50</sub> : 73.39%
<i>Menidia beryllina</i> (Growth)		>100%	100%	IC <sub>50</sub> : >100%
<i>Skeletonema</i> (Growth)		6.25%	<6.25%	IC <sub>50</sub> : 4.09%
Microtox (15 Min.)				EC <sub>50</sub> : >100%

**TABLE 5**  
**Results by Test Organism**

<i>Mysidopsis bahia</i>						
TDU I.D.	Survival (100% elutriate)	Survival (Point Estimate)	NOEC Survival	LOEC Survival	NOEC Growth	Growth IC <sub>50</sub>
TDU-1	5%	IC <sub>50</sub> : 53.13%	50%	100%	25%	>100%
TDU-2	42.5	IC <sub>50</sub> : >100%	<6.25%	>100%	100%	>100%
TDU-3	70%	IC <sub>50</sub> : >100%	<6.25%	6.25%	100%	>100%
TDU-4	50%	IC <sub>50</sub> : >100%	50%	100%	100%	>100%
<i>Menidia beryllina</i>						
TDU I.D.	Survival (100% elutriate)	Survival (Point Estimate)	NOEC Survival	LOEC Survival	NOEC Growth	Growth IC <sub>50</sub>
TDU-1	32.5%	EC <sub>50</sub> : 56.62%	6.25%	12.5%	100%	>100%
TDU-2	57.5%	EC <sub>50</sub> : >100%	50%	100%	100%	>100%
TDU-3	50%	EC <sub>50</sub> : >100%	<6.25%	6.25%	100%	>100%
TDU-4	17.5%	EC <sub>50</sub> : 73.39%	50%	100%	100%	>100%

**TABLE 6**  
**Results by Test Organism**

<i>Skeletonema costatum</i>			
TDU I.D.	NOEC Growth	LOEC Growth	Growth IC <sub>50</sub>
TDU-1	6.25%	12.5%	10.77%
TDU-2	<6.25%	6.25%	3.86%
TDU-3	<6.25%	6.25%	3.65%
TDU-4	<6.25%	6.25%	4.09%
<i>Photobacterium phosphoreum</i>			
TDU I.D.	Survival (Point Estimate)		
TDU-1	EC <sub>50</sub> : 90.2%		
TDU-2	EC <sub>50</sub> : 81.9%		
TDU-3	EC <sub>50</sub> : >81.9%		
TDU-4	EC <sub>50</sub> : >100%		

**LITERATURE CITED**

USEPA. 1991a. *Evaluation of Dredged Material Proposed for Ocean Disposal*. U.S. Environmental Protection Agency. USEPA 503/8-91/001.

USEPA. 1991b. *Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms*. USEPA 600/4-87-028.

ASTM. 1992. *Standard Guide for Conducting Static 96-h Toxicity Tests with Microalgae*. E 1218-90.

COLUMBIA ANALYTICAL SERVICES, INC.

Analytical Report

**Client:** MEC Analytical Systems, Inc.  
**Project:** NRaD Leachate/0629-001  
**Sample Matrix:** Water

**Service Request:** K9607133  
**Date Collected:** 11/4/96  
**Date Received:** 11/6/96  
**Date Extracted:** NA

Inorganic Parameters  
Units: mg/L (ppm)

Analyte:	Cyanide, Total	Phenolics, Total
EPA Method:	335.2	420.1
Method Reporting Limit:	0.01	0.01
Date Analyzed:	11/18/96	11/15/96

Sample Name	Lab Code		
C961101.04	K9607133-001	ND	ND
C961101.05	K9607133-002	ND	ND
C961101.06	K9607133-003	ND	0.05
C961101.07	K9607133-004	ND	ND
Method Blank	K9607133-MB	ND	ND

Approved By: \_\_\_\_\_

*Henry Phillips*

Date: 11/20/96

**COLUMBIA ANALYTICAL SERVICES, INC.**

**Analytical Report**


**Client:** MEC Analytical Systems, Inc.  
**Project:** NRaD Leachate/0629-001  
**Sample Matrix:** Water

**Service Request:** K9607133  
**Date Collected:** 11/4/96  
**Date Received:** 11/6/96  
**Date Extracted:** 11/7/96

Total Toxic Organics (TTO)  
 Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs)  
 EPA Methods 3520B/608  
 Units: µg/L (ppb)

<b>Sample Name:</b>	<b>C961101.04</b>	<b>C961101.05</b>	<b>C961101.06</b>
<b>Lab Code:</b>	K9607133-001	K9607133-002	K9607133-003
<b>Date Analyzed:</b>	11/18,19/96	11/19/96	11/19/96

<b>Analyte</b>	<b>MRL</b>			
alpha-BHC	0.04	ND	ND	ND
beta-BHC	0.04	ND	ND	ND
gamma-BHC (Lindane)	0.04	ND	ND	ND
delta-BHC	0.04	ND	ND	ND
Heptachlor	0.04	ND	ND	ND
Aldrin	0.04	ND	ND	ND
Heptachlor Epoxide	0.04	ND	ND	ND
Endosulfan I	0.04	ND	ND	ND
Dieldrin	0.04	ND	ND	ND
4,4'-DDE	0.04	ND	ND	ND
Endrin	0.04	ND	ND	ND
Endosulfan II	0.04	ND	ND	ND
4,4'-DDD	0.04	ND	ND	ND
Endrin Aldehyde	0.04	ND	ND	ND
Endosulfan Sulfate	0.04	ND	ND	ND
4,4'-DDT	0.04	ND	ND	ND
Toxaphene	1	ND	ND	ND
Chlordane	0.5	ND	ND	ND
Aroclor 1016	0.2	ND	ND	ND
Aroclor 1221	0.2	ND	ND	ND
Aroclor 1232	0.2	ND	ND	ND
Aroclor 1242	0.2	ND	ND	ND
Aroclor 1248	0.2	ND	ND	ND
Aroclor 1254	0.2	ND	ND	ND
Aroclor 1260	0.2	ND	ND	ND

Approved By: 

Date: 11/21/96

# COLUMBIA ANALYTICAL SERVICES, INC.

## Analytical Report

**Client:** MEC Analytical Systems, Inc.  
**Project:** NRaD Leachate/0629-001  
**Sample Matrix:** Water

**Service Request:** K9607133  
**Date Collected:** 11/4/96  
**Date Received:** 11/6/96  
**Date Extracted:** 11/7/96

Total Toxic Organics (TTO)  
 Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs)  
 EPA Methods 3520B/608  
 Units: µg/L (ppb)

Sample Name:	C961101.07	Method Blank
Lab Code:	K9607133-004	K961107-WB
Date Analyzed:	11/19/96	11/18,19/96

Analyte	MRL		
alpha-BHC	0.04	ND	ND
beta-BHC	0.04	ND	ND
gamma-BHC (Lindane)	0.04	ND	ND
delta-BHC	0.04	ND	ND
Heptachlor	0.04	ND	ND
Aldrin	0.04	ND	ND
Heptachlor Epoxide	0.04	ND	ND
Endosulfan I	0.04	ND	ND
Dieldrin	0.04	ND	ND
4,4'-DDE	0.04	ND	ND
Endrin	0.04	ND	ND
Endosulfan II	0.04	ND	ND
4,4'-DDD	0.04	ND	ND
Endrin Aldehyde	0.04	ND	ND
Endosulfan Sulfate	0.04	ND	ND
4,4'-DDT	0.04	ND	ND
Toxaphene	1	ND	ND
Chlordane	0.5	ND	ND
Aroclor 1016	0.2	ND	ND
Aroclor 1221	0.2	ND	ND
Aroclor 1232	0.2	ND	ND
Aroclor 1242	0.2	ND	ND
Aroclor 1248	0.2	ND	ND
Aroclor 1254	0.2	ND	ND
Aroclor 1260	0.2	ND	ND

Approved By: \_\_\_\_\_

Date: 11/21/96



## COLUMBIA ANALYTICAL SERVICES, INC.

## Analytical Report

Client: MEC Analytical Systems, Inc.  
Project: NRaD Leachate/ #0629-001  
Sample Matrix: Water

Service Request: K9607133  
Date Collected: 11/4/96  
Date Received: 11/6/96  
Date Extracted: NA

Total Toxic Organics (TTO)  
Volatile Organic Compounds  
EPA Method 624  
Units: µg/L (ppb)

Sample Name:	C961101.04	C961101.05	C961101.06
Lab Code:	K9607133-001	K9607133-002	K9607133-003
Date Analyzed:	11/7/96	11/7/96	11/7/96

Analyte	MRL			
Chloromethane	10	ND	ND	ND
Vinyl Chloride	10	ND	ND	ND
Bromomethane	10	ND	ND	ND
Chloroethane	10	ND	ND	ND
1,1-Dichloroethene (1,1-DCE)	5	ND	ND	ND
Methylene Chloride	5	ND	ND	ND
trans-1,2-Dichloroethene	5	ND	ND	ND
1,1-Dichloroethane	5	ND	ND	ND
Chloroform	5	ND	ND	ND
1,1,1-Trichloroethane (TCA)	5	ND	ND	ND
Carbon Tetrachloride	5	ND	ND	ND
Benzene	5	ND	ND	ND
1,2-Dichloroethane	5	ND	ND	ND
Trichloroethene (TCE)	5	ND	ND	ND
1,2-Dichloropropane	5	ND	ND	ND
Bromodichloromethane	5	ND	ND	ND
2-Chloroethyl Vinyl Ether	10	ND	ND	ND
Total-1,3-Dichloropropylene	5	ND	ND	ND
Toluene	5	ND	ND	ND
1,1,2-Trichloroethane	5	ND	ND	ND
Tetrachloroethene (PCE)	5	ND	ND	ND
Dibromochloromethane	5	ND	ND	ND
Chlorobenzene	5	ND	ND	ND
Ethylbenzene	5	ND	ND	ND
Bromoform	5	ND	ND	ND
1,1,2,2-Tetrachloroethane	5	ND	ND	ND
1,3-Dichlorobenzene	5	ND	ND	ND
1,4-Dichlorobenzene	5	ND	ND	ND
1,2-Dichlorobenzene	5	ND	ND	ND
Acrolein	100	ND	ND	ND
Acrylonitrile	10	ND	ND	ND

Approved By: \_\_\_\_\_

Date: \_\_\_\_\_

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## COLUMBIA ANALYTICAL SERVICES, INC.

## Analytical Report

**Client:** MEC Analytical Systems, Inc.  
**Project:** NRaD Leachate/ #0629-001  
**Sample Matrix:** Water

**Service Request:** K9607133  
**Date Collected:** 11/4/96  
**Date Received:** 11/6/96  
**Date Extracted:** NA

Total Toxic Organics (TTO)  
 Volatile Organic Compounds  
 EPA Method 624  
 Units: µg/L (ppb)

Sample Name: C961101.07      Method Blank  
 Lab Code: K9607133-004      K961106-MB  
 Date Analyzed: 11/7/96      11/6/96

Analyte	MRL		
Chloromethane	10	ND	ND
Vinyl Chloride	10	ND	ND
Bromomethane	10	ND	ND
Chloroethane	10	ND	ND
1,1-Dichloroethene (1,1-DCE)	5	ND	ND
Methylene Chloride	5	ND	ND
<i>trans</i> -1,2-Dichloroethene	5	ND	ND
1,1-Dichloroethane	5	ND	ND
Chloroform	5	ND	ND
1,1,1-Trichloroethane (TCA)	5	ND	ND
Carbon Tetrachloride	5	ND	ND
Benzene	5	ND	ND
1,2-Dichloroethane	5	ND	ND
Trichloroethene (TCE)	5	ND	ND
1,2-Dichloropropane	5	ND	ND
Bromodichloromethane	5	ND	ND
2-Chloroethyl Vinyl Ether	10	ND	ND
Total-1,3-Dichloropropylene	5	ND	ND
Toluene	5	ND	ND
1,1,2-Trichloroethane	5	ND	ND
Tetrachloroethene (PCE)	5	ND	ND
Dibromochloromethane	5	ND	ND
Chlorobenzene	5	ND	ND
Ethylbenzene	5	ND	ND
Bromoform	5	ND	ND
1,1,2,2-Tetrachloroethane	5	ND	ND
1,3-Dichlorobenzene	5	ND	ND
1,4-Dichlorobenzene	5	ND	ND
1,2-Dichlorobenzene	5	ND	ND
Acrolein	100	ND	ND
Acrylonitrile	10	ND	ND

Approved By: \_\_\_\_\_

C. Haines

Date: \_\_\_\_\_

11/13/96

## COLUMBIA ANALYTICAL SERVICES, INC.

## Analytical Report


Client: MEC Analytical Systems, Inc.  
Project: NRaD Leachate/0629-001  
Sample Matrix: Water

Service Request: K9607133  
Date Collected: 11/4/96  
Date Received: 11/6/96  
Date Extracted: 11/7/96

Total Toxic Organics (TTO)  
Semivolatile Organic Compounds  
EPA Method 625  
Units: µg/L (ppb)

Sample Name:	C961101.04	C961101.05	C961101.06
Lab Code:	K9607133-001	K9607133-002	K9607133-003
Date Analyzed:	11/19/96	11/19/96	11/19/96

Base Neutral Analyte	MRL			
N-Nitrosodimethylamine	25	ND	ND	ND
Bis(2-chloroethyl) Ether	10	ND	ND	ND
Bis(2-chloroisopropyl) Ether	10	ND	ND	ND
N-Nitrosodi-n-propylamine	10	ND	ND	ND
Hexachloroethane	10	ND	ND	ND
Nitrobenzene	10	ND	ND	ND
Isophorone	10	ND	ND	ND
Bis(2-chloroethoxy)methane	10	ND	ND	ND
1,2,4-Trichlorobenzene	10	ND	ND	ND
Naphthalene	10	ND	ND	ND
Hexachlorobutadiene	10	ND	ND	ND
Hexachlorocyclopentadiene	10	ND	ND	ND
2-Chloronaphthalene	10	ND	ND	ND
Dimethyl Phthalate	10	11	ND	ND
Acenaphthylene	10	ND	ND	ND
Acenaphthene	10	ND	ND	ND
2,4-Dinitrotoluene	10	ND	ND	ND
2,6-Dinitrotoluene	10	ND	ND	ND
Diethyl Phthalate	10	ND	ND	ND
4-Chlorophenyl Phenyl Ether	10	ND	ND	ND
Fluorene	10	ND	ND	ND
N-Nitrosodiphenylamine	10	ND	ND	ND

Approved By: 

Date: 11.21.96

## COLUMBIA ANALYTICAL SERVICES, INC.

## Analytical Report

Client: MEC Analytical Systems, Inc.  
 Project: NRaD Leachate/0629-001  
 Sample Matrix: Water

Service Request: K9607133  
 Date Collected: 11/4/96  
 Date Received: 11/6/96  
 Date Extracted: 11/7/96

Total Toxic Organics (TTO)  
 Semivolatile Organic Compounds  
 EPA Method 625  
 Units: µg/L (ppb)

Sample Name:	C961101.04	C961101.05	C961101.06
Lab Code:	K9607133-001	K9607133-002	K9607133-003
Date Analyzed:	11/19/96	11/19/96	11/19/96

Base Neutral Analyte	MRL			
4-Bromophenyl Phenyl Ether	10	ND	ND	ND
Hexachlorobenzene	10	ND	ND	ND
Phenanthrene	10	ND	ND	ND
Anthracene	10	ND	ND	ND
Di-n-butyl Phthalate	10	ND	ND	ND
Fluoranthene	10	ND	ND	ND
Pyrene	10	ND	ND	ND
Butylbenzyl Phthalate	10	ND	ND	ND
3,3'-Dichlorobenzidine	25	ND	ND	ND
Benz(a)anthracene	10	ND	ND	ND
Bis(2-ethylhexyl) Phthalate	10	ND	15	ND
Chrysene	10	ND	ND	ND
Di-n-octyl Phthalate	10	ND	ND	ND
Benzo(b)fluoranthene	10	ND	ND	ND
Benzo(k)fluoranthene	10	ND	ND	ND
Benzo(a)pyrene	10	ND	ND	ND
Indeno(1,2,3-cd)pyrene	10	ND	ND	ND
Dibenz(a,h)anthracene	10	ND	ND	ND
Benzo(g,h,i)perylene	10	ND	ND	ND
Benztidine	25	ND	ND	ND
1,2-Diphenylhydrazine*	10	ND	ND	ND
2,3,7,8-TCDD**	50	ND	ND	ND

\* Analyzed as azobenzene.

\*\* 2,3,7,8-Tetrachlorodibenzo-p-dioxin searched for as a tentatively identified compound.

Approved By: 

Date: 11.21.96

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**COLUMBIA ANALYTICAL SERVICES, INC.**

Analytical Report

**Client:** MEC Analytical Systems, Inc.  
**Project:** NRaD Leachate/0629-001  
**Sample Matrix:** Water

**Service Request:** K9607133  
**Date Collected:** 11/4/96  
**Date Received:** 11/6/96  
**Date Extracted:** 11/7/96

Total Toxic Organics (TTO)  
 Semivolatile Organic Compounds  
 EPA Method 625  
 Units: µg/L (ppb)

Sample Name:	<b>C961101.04</b>	<b>C961101.05</b>	<b>C961101.06</b>
Lab Code:	K9607133-001	K9607133-002	K9607133-003
Date Analyzed:	11/19/96	11/19/96	11/19/96

Acid Analyte	MRL			
Phenol	10	ND	ND	34
2-Chlorophenol	10	ND	ND	ND
2-Nitrophenol	10	ND	ND	ND
2,4-Dimethylphenol	10	ND	ND	ND
2,4-Dichlorophenol	10	ND	ND	ND
4-Chloro-3-methylphenol	10	ND	ND	ND
2,4,6-Trichlorophenol	10	ND	ND	ND
2,4-Dinitrophenol	25	ND	ND	ND
4-Nitrophenol	25	ND	ND	ND
2-Methyl-4,6-dinitrophenol	25	ND	ND	ND
Pentachlorophenol	25	ND	ND	ND

Approved By: \_\_\_\_\_

Date: 11-21-96

## COLUMBIA ANALYTICAL SERVICES, INC.

## Analytical Report

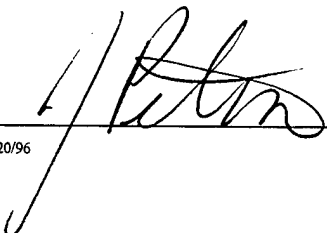
Client: MEC Analytical Systems, Inc.  
Project: NRaD Leachate/0629-001  
Sample Matrix: Water

Service Request: K9607133  
Date Collected: 11/4/96  
Date Received: 11/6/96  
Date Extracted: 11/7/96

Total Toxic Organics (TTO)  
Semivolatile Organic Compounds  
EPA Method 625  
Units: µg/L (ppb)

Sample Name: C961101.07      Method Blank  
Lab Code: K9607133-004      K961107-WB1  
Date Analyzed: 11/19/96      11/19/96

Base Neutral Analyte	MRL		
N-Nitrosodimethylamine	25	ND	ND
Bis(2-chloroethyl) Ether	10	ND	ND
Bis(2-chloroisopropyl) Ether	10	ND	ND
N-Nitrosodi-n-propylamine	10	ND	ND
Hexachloroethane	10	ND	ND
Nitrobenzene	10	ND	ND
Isophorone	10	ND	ND
Bis(2-chloroethoxy)methane	10	ND	ND
1,2,4-Trichlorobenzene	10	ND	ND
Naphthalene	10	ND	ND
Hexachlorobutadiene	10	ND	ND
Hexachlorocyclopentadiene	10	ND	ND
2-Chloronaphthalene	10	ND	ND
Dimethyl Phthalate	10	ND	ND
Acenaphthylene	10	ND	ND
Acenaphthene	10	ND	ND
2,4-Dinitrotoluene	10	ND	ND
2,6-Dinitrotoluene	10	ND	ND
Diethyl Phthalate	10	ND	ND
4-Chlorophenyl Phenyl Ether	10	ND	ND
Fluorene	10	ND	ND
N-Nitrosodiphenylamine	10	ND	ND

Approved By: 

Date: 11-21-96

## COLUMBIA ANALYTICAL SERVICES, INC.

## Analytical Report

Client: MEC Analytical Systems, Inc.  
Project: NRaD Leachate/0629-001  
Sample Matrix: Water

Service Request: K9607133  
Date Collected: 11/4/96  
Date Received: 11/6/96  
Date Extracted: 11/7/96

Total Toxic Organics (TTO)  
Semivolatile Organic Compounds  
EPA Method 625  
Units: µg/L (ppb)

Sample Name: C961101.07      Method Blank  
Lab Code: K9607133-004      K961107-WB1  
Date Analyzed: 11/19/96      11/19/96

Base Neutral Analyte	MRL		
4-Bromophenyl Phenyl Ether	10	ND	ND
Hexachlorobenzene	10	ND	ND
Phenanthrene	10	ND	ND
Anthracene	10	ND	ND
Di- <i>n</i> -butyl Phthalate	10	ND	ND
Fluoranthene	10	ND	ND
Pyrene	10	ND	ND
Butylbenzyl Phthalate	10	ND	ND
3,3'-Dichlorobenzidine	25	ND	ND
Benz(a)anthracene	10	ND	ND
Bis(2-ethylhexyl) Phthalate	10	ND	ND
Chrysene	10	ND	ND
Di- <i>n</i> -octyl Phthalate	10	ND	ND
Benzo(b)fluoranthene	10	ND	ND
Benzo(k)fluoranthene	10	ND	ND
Benzo(a)pyrene	10	ND	ND
Indeno(1,2,3-cd)pyrene	10	ND	ND
Dibenz(a,h)anthracene	10	ND	ND
Benzo(g,h,i)perylene	10	ND	ND
Benzidine	25	ND	ND
1,2-Diphenylhydrazine*	10	ND	ND
2,3,7,8-TCDD**	50	ND	ND

\* Analyzed as azobenzene.

\*\* 2,3,7,8-Tetrachlorodibenzo-p-dioxin searched for as a tentatively identified compound.

Approved By: 

Date: 11-21-96

07133SVM.JS1 - 4,MB 11/20/96

Page No.:

00012

COLUMBIA ANALYTICAL SERVICES, INC.

Analytical Report

Client: MEC Analytical Systems, Inc.  
Project: NRaD Leachate/0629-001  
Sample Matrix: Water

Service Request: K9607133  
Date Collected: 11/4/96  
Date Received: 11/6/96  
Date Extracted: 11/7/96

Total Toxic Organics (TTO)  
Semivolatile Organic Compounds  
EPA Method 625  
Units: µg/L (ppb)

Sample Name: C961101.07      Method Blank  
Lab Code: K9607133-004      K961107-WB1  
Date Analyzed: 11/19/96      11/19/96

Acid Analyte	MRL		
Phenol	10	ND	ND
2-Chlorophenol	10	ND	ND
2-Nitrophenol	10	ND	ND
2,4-Dimethylphenol	10	ND	ND
2,4-Dichlorophenol	10	ND	ND
4-Chloro-3-methylphenol	10	ND	ND
2,4,6-Trichlorophenol	10	ND	ND
2,4-Dinitrophenol	25	ND	ND
4-Nitrophenol	25	ND	ND
2-Methyl-4,6-dinitrophenol	25	ND	ND
Pentachlorophenol	25	ND	ND

Approved By: 

Date: 11.21.96

3S3PBNA/102094

07133SVM.JS1 - 4,MB 11/20/96

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00013



**APPENDIX A**  
**LABORATORY QC RESULTS**

COLUMBIA ANALYTICAL SERVICES, INC.

QA/QC Report


Client: MEC Analytical Systems, Inc.  
Project: NRaD Leachate/0629-001  
Sample Matrix: Water

Service Request: K9607133  
Date Collected: 11/4/96  
Date Received: 11/6/96  
Date Extracted: 11/7/96  
Date Analyzed: 11/18,19/96

Surrogate Recovery Summary  
Total Toxic Organics (TTO)  
Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs)  
EPA Methods 3520B/608

Sample Name	Lab Code	Percent Recovery	Percent Recovery
		Tetrachloro- <i>m</i> -xylene	Decachlorobiphenyl
C961101.04	K9607133-001	49	53
C961101.05	K9607133-002	62	76
C961101.06	K9607133-003	37	56
C961101.07	K9607133-004	45	46
Method Blank	K961107-WB	62	93

CAS Acceptance Limits: 20-100 33-137

Approved By: 

Date: 11/21/96

**COLUMBIA ANALYTICAL SERVICES, INC.**

**QA/QC Report**

**Client:** MEC Analytical Systems, Inc.  
**Project:** NRaD Leachate/ #0629-001  
**Sample Matrix:** Water

**Service Request:** K9607133  
**Date Collected:** 11/4/96  
**Date Received:** 11/6/96  
**Date Extracted:** NA  
**Date Analyzed:** 11/6,7/96

Surrogate Recovery Summary  
 Volatile Organic Compounds  
 EPA Method 624

Sample Name	Lab Code	P e r c e n t   R e c o v e r y		
		1,2-Dichloroethane - <i>d</i> <sub>4</sub>	Toluene- <i>d</i> <sub>8</sub>	4-Bromofluorobenzene
C961101.04	K9607133-001	99	100	94
C961101.05	K9607133-002	97	96	91
C961101.06	K9607133-003	98	94	90
C961101.07	K9607133-004	99	97	90
Method Blank	K961106-MB	97	102	100

CAS Acceptance Limits:    87-117                      93-109                      85-111

Approved By: \_\_\_\_\_

*CC Lewis*

Date: \_\_\_\_\_

*11/13/96*

## COLUMBIA ANALYTICAL SERVICES, INC.

## QA/QC Report

Client: MEC Analytical Systems, Inc.  
Project: NRaD Leachate/0629-001  
Sample Matrix: Water

Service Request: K9607133  
Date Collected: 11/4/96  
Date Received: 11/6/96  
Date Extracted: 11/7/96  
Date Analyzed: 11/19/96

Surrogate Recovery Summary  
Total Toxic Organics (TTO)  
Semivolatile Organic Compounds  
EPA Method 625

Sample Name	Lab Code	P e r c e n t R e c o v e r y					
		2FP	PHL	TBP	NBZ	FBP	TPH
C961101.04	K9607133-001	61	78	74	78	74	70
C961101.05	K9607133-002	69	90	65	94	86	75
C961101.06	K9607133-003	77	98	79	102 A	89	76
C961101.07	K9607133-004	67	88	71	93	80	72
Method Blank	K961107-WB1	70	88	61	87	93	151 A

CAS Acceptance Limits: 23-98 D-114 36-120 42-100 45-99 1-128

2FP 2-Fluorophenol  
PHL Phenol-*d*<sub>6</sub>  
TBP 2,4,6-Tribromophenol  
NBZ Nitrobenzene-*d*<sub>5</sub>  
FBP 2-Fluorobiphenyl  
TPH Terphenyl-*d*<sub>14</sub>

A Outside acceptance limits; see case narrative.

Approved By: 

Date: 11-21-96

SUR6X/111594

07133SVM.JS1 - SUR 11/20/96

00017

## Analytical Report

**Service Request:** K9607298  
**Date Collected:** 11/12/96  
**Date Received:** 11/13/96  
**Date Extracted:** 11/14/96

Sample Name:	C961101-04	C961101-05	C961101-06
Lab Code:	K9607298-001	K9607298-002	K9607298-003
Date Analyzed:	11/20/96	11/20/96	11/20/96

Analyte	EPA		California		
	Method	MRL	Method	MRL	Method
Antimony	6010A	50	ND	ND	ND
Arsenic	7060	5	ND	ND	ND
Beryllium	6010A	5	ND	ND	ND
Cadmium	6010A	4	<10(C)	<10(C)	<10(C)
Chromium	6010A	5	<10(C)	<10(C)	<10(C)
Copper	6010A	10	191	ND	ND
Lead	7421	2	<5(D)	<5(D)	<5(D)
Mercury	7470	0.5	ND	ND	ND
Nickel	6010A	20	<40(C)	<40(C)	<40(C)
Selenium	7740	5	<10(D)	<10(D)	<10(D)
Silver	6010A	10	ND	ND	ND
Thallium	7841	5	<10(D)	<10(D)	<10(D)
Zinc	6010A	10	23	21	23

B The MRL is elevated because of matrix interferences.

D The MRL is elevated because of matrix interferences and because the sample required diluting.

Approved By:

3S30EPA/102094

07298ICP.JC1 - Sample 11/20/96

Date: 11/20/96

Page No  
**00003**

**COLUMBIA ANALYTICAL SERVICES, INC.**

Analytical Report

**Client:** MEC Analytical Systems, Inc.  
**Project:** NRaD  
**Sample Matrix:** Water

**Service Request:** K9607298  
**Date Collected:** 11/12/96  
**Date Received:** 11/13/96  
**Date Extracted:** 11/14/96

Total Metals  
 Units: µg/L (ppb)

<b>Sample Name:</b>	<b>C961101-07</b>	<b>Method Blank</b>
<b>Lab Code:</b>	K9607298-004	K9607298-MB
<b>Date Analyzed:</b>	11/20/96	11/20/96

Analyte	EPA	MRL		
	Method			
Antimony	6010A	50	ND	ND
Arsenic	7060	5	ND	ND
Beryllium	6010A	5	ND	ND
Cadmium	6010A	4	<10(C)	ND
Chromium	6010A	5	<10(C)	ND
Copper	6010A	10	ND	ND
Lead	7421	2	<5(D)	ND
Mercury	7470	0.5	ND	ND
Nickel	6010A	20	<40(C)	ND
Selenium	7740	5	<10(D)	ND
Silver	6010A	10	ND	ND
Thallium	7841	5	<10(D)	ND
Zinc	6010A	10	21	ND

B The MRL is elevated because of matrix interferences.  
 D The MRL is elevated because of matrix interferences and because the sample required diluting.

Approved By: \_\_\_\_\_ Date: 11/20/96

## **Appendix B**

### **QWIKLITE BIOASSAY ANALYSES**

Source: Naval Command, Control, & Ocean Surveillance Center,  
RDTE Division, Code D362

**MARINE ACUTE TOXICITY RESULTS OF TRASH DISPOSAL  
UNITS (TDU) TO MARINE DINOFLAGELLATE (*GONYAULAX*  
*POLYEDRA*)**

By

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December 1996

A report prepared for:

Chuck Katz



## **INTRODUCTION**

A series of QwikLite Bioluminescence Assays were conducted to assess the potential toxicity of various Trash Disposal Units (TDU) and their contents discharged into the ocean, and its potential impact on marine organisms. A total of eight samples were tested; four TDU leachates (TDU 12, 13, 15, and 16) were prepared by MEC Analytical Systems, Inc. and the remaining four leachates made from TDU 14 and TDU 17, were samples taken from inside the canister and 0.5m away from the container surface after leaching for 24 hours. Each leachate was tested on the bioluminescent dinoflagellate *Gonyaulax polyedra*. The endpoints measured were the concentration at which 50% of test organisms were affected (IC50) and the concentration at which no observable effect occurred (NOEC). Effects of potential toxicity in the effluents could be observed by inhibition of bioluminescence in the dinoflagellates.

## **MATERIALS AND METHODS**

### **Test Equipment**

The QwikLite bioluminescent assays involved the use of spectrophotometric grade cuvettes to contain approximately three ml of test solution and dinoflagellates. Each cuvette was placed in the QwikLite test chamber where bioluminescence from each test solution was measured. All cuvettes used were new and soaked in deionized water prior to use. All glassware used was washed with 10% Nitric Acid, saturated Potassium Hydroxide (KOH), and rinsed thoroughly with deionized water in between and after each cleaning.

### **Source and Acclimation of Test Species**

Cultures of *Gonyaulax polyedra* were maintained in pre-soaked Erlenmeyer flasks in Enriched Saltwater Medium at 19 °C. Cultures were placed on a 12:12 hour (day/night) light schedule under cool white fluorescent bulbs at a light intensity of approximately 4000 lux.

### **Test Sample Preparation**

TDU 12, 13, 15, and 16 were leachates prepared by MEC Analytical Systems, Inc., containing a 20% (1:4 sample to seawater) elutriate and stored in five gallon polyethylene containers. TDU 14 and 17 were seawater samples collected from inside the canister and from 0.5m away from the container surface which was placed in San Diego Bay and leached for 24 hours. These leachates were collected and stored in one liter polycarbonate containers. Each test sample was defrosted at room temperature 24 hours before testing and filtered to 0.45  $\mu$ m. For testing purposes and to determine a dose response curve, the 100% test sample was diluted with filtered sea water to 6.25%. The test concentrations for each assay were 100%, 50%, 25%, 12.5%, and 6.25%, or ranged from 25% to 1.5625% leachate. For further analysis, each filtered leachate (100%) was analyzed for ammonia, in the form of ammonia nitrogen ( $\text{NH}_3\text{-N}$ ), using the HACH DR/2000 Spectrophotometer.

### **Experimental Test Design for QwikLite (Bioluminescence) Bioassay System**

The QwikLite Bioassay measures the inhibition of light emitted by the bioluminescent dinoflagellate, *Gonyaulax polyedra*, exposed to a test solution. The test lasts 96 hours and results are expressed as the percent of control in which all dilutions are compared to the controls. Toxicity results are reported as the IC<sub>50</sub> when a dose response is exhibited. Testing of the dinoflagellate is accomplished by placing individual cuvettes containing the test material, media, and cells into a darkened test chamber which is attached to a photomultiplier tube (PMT). The QwikLite bioassay system uses a 2-inch diameter 8575 PMT with an S-20 response used in the photon count mode. The top of the test chamber is removable and houses a small adjustable motor which drives a stainless steel shaft terminating in a plastic propeller. The propeller is seated into the cuvette and as the contents are stirred, bioluminescence is generated and measured by the PMT. Each test period is completed at 24 hour intervals thereafter until completion of the bioassay. Mean light output (PMT counts) is calculated for each experimental group and control. Light

output means are then graphed as light output (percent of control) as a function of time. All graphs represent the data collected at 96 hours of exposure.

## RESULTS

Effects of TDU leachate to *Gonyaulax polyedra*:

### TDU 12

This assay resulted in a dose response curve and an IC50 value of 4.3% (Figure 1). After 96 hours, no NOEC value was applicable (less than 6.25%). High ammonia levels averaging 765 ppb were measured in the 100% filtered leachate (Table 1).

### TDU 13

This assay resulted in a dose response curve where the IC50 value at 96 hours of exposure was observed at 12.7% (Figure 2). High ammonia values (average = 1386 ppb) were measured in the 100% filtered leachate (Table 1).

### TDU 15

This assay resulted in a dose response curve with an IC50 value of 20.5% after 96 hours of exposure (Figure 3). Low values of ammonia were detected in the 100% filtered leachate (Table 1).

### TDU 16

This assay resulted in a dose response curve after 96 hours of exposure and an IC50 value of 10.8% (Figure 4). Ammonium levels averaging 270 ppb were reported in the 100% filtered leachate (Table 1).

### TDU 14 Inside Canister

This assay resulted in a dose response curve with an IC50 value of 77.3% (Figure 5). After 96 hours of exposure, a NOEC value was observed at 50% leachate. Low values of ammonia were reported in the 100% filtered leachate (Table 1).

### TDU 14 Outside Canister, 0.5m away

This assay resulted in a slight hormesis or enhancement of bioluminescence above control with no observable IC50 (Figure 6). After 96 hours of exposure, the NOEC value was greater than 100%. The levels of ammonia detected were low in the 100% filtered leachate (Table 1).

#### TDU 17 Inside Canister

This assay resulted in a dose response curve with an IC50 value of 63.7% (Figure 7). A slight hormesis or enhancement of bioluminescence above control at 6.25%, 12.5%, and 25% leachate were observed. An NOEC value of 25% was observed after 96 hours of exposure. Low ammonium values in the 100% filtered leachate were detected (Table 1).

#### TDU 17 Outside Canister, 0.5m away

One assay resulted in no inhibition or enhancement of bioluminescence (Figure 8); no IC50 was observable in *Gonyaulax polyedra* from this effluent. After 96 hours of exposure the NOEC value was greater than the 100% leachate. Ammonia levels were low in the 100% filtered leachate (Table 1).

### DISCUSSION

#### **Biological Analyses**

Eight acute toxicity tests were conducted with *Gonyaulax polyedra*.

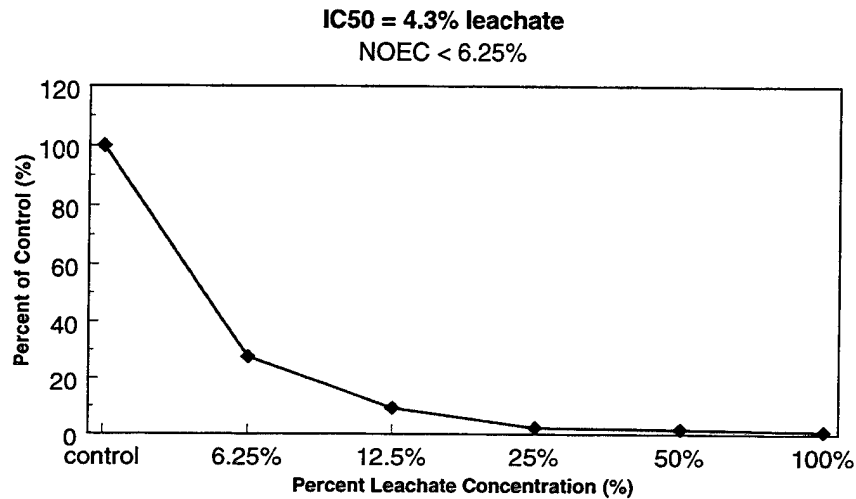
Bioluminescence inhibition was observed in *Gonyaulax polyedra* when exposed to TDUs 12, 13, 15, and 16 leachates. IC50 values ranged from 4% (TDU 12) to 20% (TDU 15). NOEC values were less than 6.25% in TDUs 12, 13, 15, and 16. Ammonia's presence is important to note in TDUs 2, 3, and 4 as values averaged from 270-1386 ppb (Table 1). Results from reference toxicant testing using NH<sub>3</sub>Cl on *Gonyaulax polyedra*, produced IC50 values at a concentration of approximately 200 ppb. It is possible that the toxic effects observed on *Gonyaulax polyedra* from TDUs 12, 13, and 16 are a direct result of high levels of ammonia. In TDU 15 ammonia levels were significantly lower (average = 13 ppb), yet toxicity was observed. When TDUs 12, 13, 15, and 16, were analyzed for metals, copper was found only in TDU 15 (191 ppb) ("Elutriate Toxicity Testing of Trash Disposal Units", MEC Analytical Systems, Inc.). Results from reference toxicant using copper sulfate as the toxicant on *Gonyaulax*, produced IC50 values at a concentration of approximately 20 ppb. Thus, it is possible that the toxic effects from TDU 15 observed in *Gonyaulax* are a result of high concentrations of copper.

The remaining four acute toxicity tests were performed for TDU 14 inside and outside the container and TDU 17 inside and outside the container. Toxicity was observed in *Gonyaulax* when exposed to TDU 14 and 17 leachates from inside the container. IC50 values were 77 % and 64% leachates and NOEC values of 50% and 25% inside for TDU 14 and 17, respectively. Test samples taken outside the container, 0.5 m away, showed no measurable toxicity with an IC50 greater than 100% and NOEC values of greater than the 100% leachate.

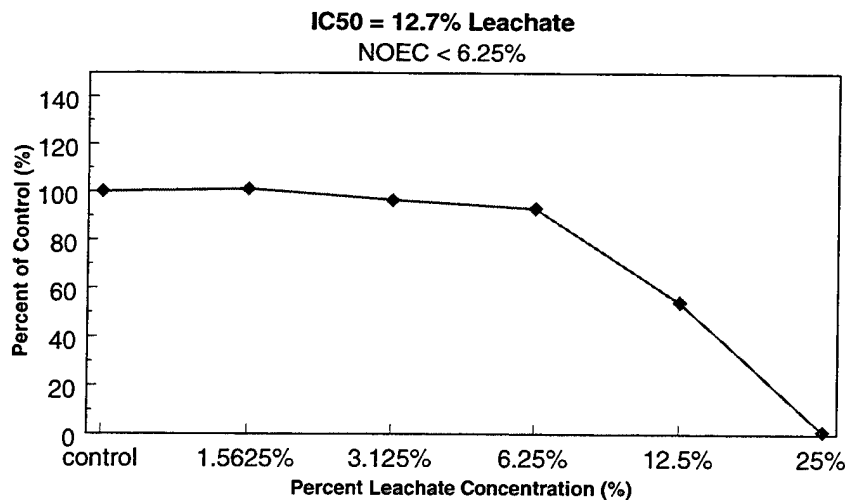
**Table 1**  
**Summary of TDU samples**

<b>Sample (100% Leachate)</b>	<b>IC50</b>	<b>NOEC</b>	<b>Ammonia (ppb)</b>
<b>TDU 12</b>	<b>4.3%</b>	<b>&lt; 6.25%</b>	<b>765 ppb</b>
<b>TDU 13</b>	<b>12.7%</b>	<b>&lt; 6.25%</b>	<b>1386 ppb</b>
<b>TDU 15</b>	<b>20.5%</b>	<b>3.125%</b>	<b>13 ppb</b>
<b>TDU 16</b>	<b>10.8%</b>	<b>&lt; 6.25%</b>	<b>270 ppb</b>
<b>TDU 14 inside canister</b>	<b>77.3%</b>	<b>50%</b>	<b>0.5 ppb</b>
<b>TDU 14 outside canister</b>	<b>No IC50</b>	<b>&gt; 100%</b>	<b>2.2 ppb</b>
<b>TDU 17 inside canister</b>	<b>63.7%</b>	<b>25%</b>	<b>4.9 ppb</b>
<b>TDU 17 outside canister</b>	<b>No IC50</b>	<b>&gt; 100%</b>	<b>0.8 ppb</b>

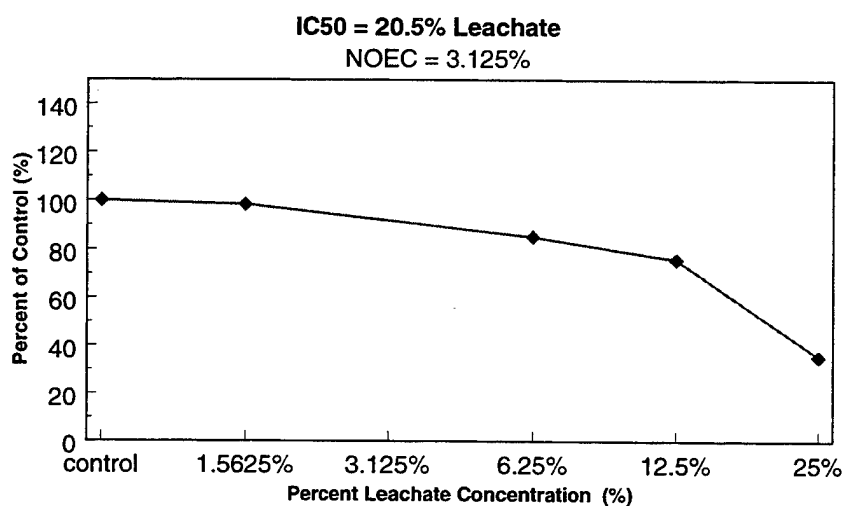
**Figure 1. TDU 12 - 100% Leachate**  
***Gonyaulax polyedra***



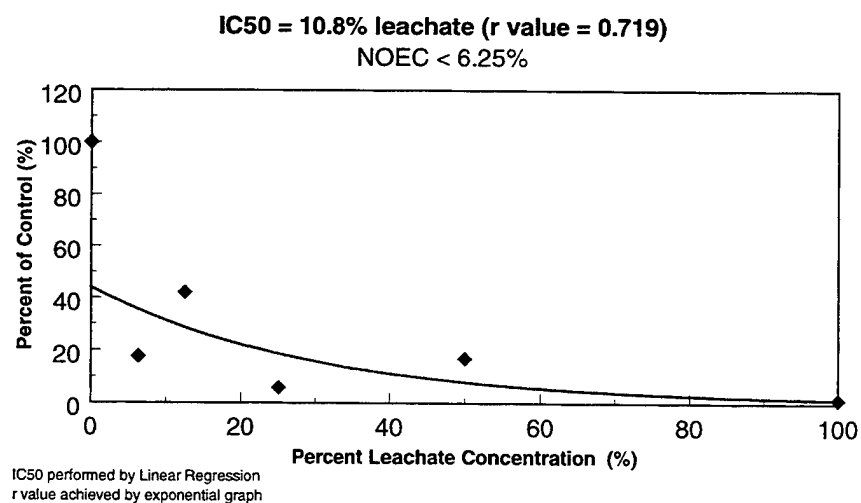
**Figure 2. TDU 13 - 100% Leachate**  
***Gonyaulax polyedra***



**Figure 3. TDU 15 - 100% Leachate**  
***Gonyaulax polyedra***



**Figure 4. TDU 16 - 100% Leachate**  
***Gonyaulax polyedra***



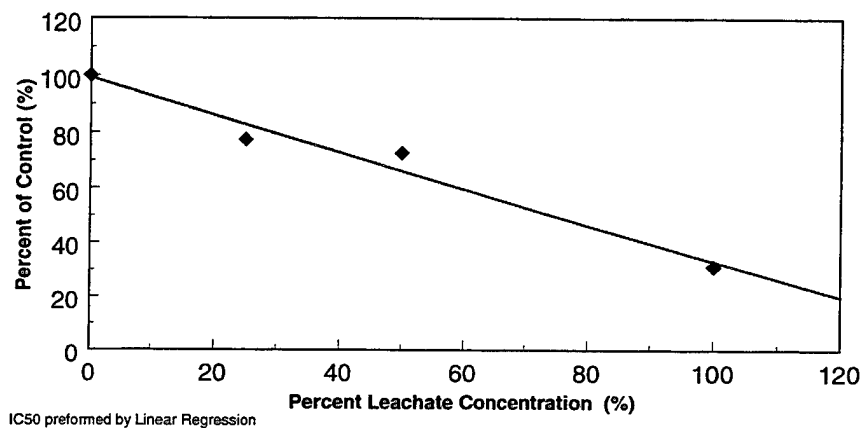


**Figure 5. TDU 14 - 100% Leachate Inside Canister**

***Gonyaulax Polyedra***

IC50 = 77.3% Leachate (r value = 0.97)

NOEC = 50% Leachate

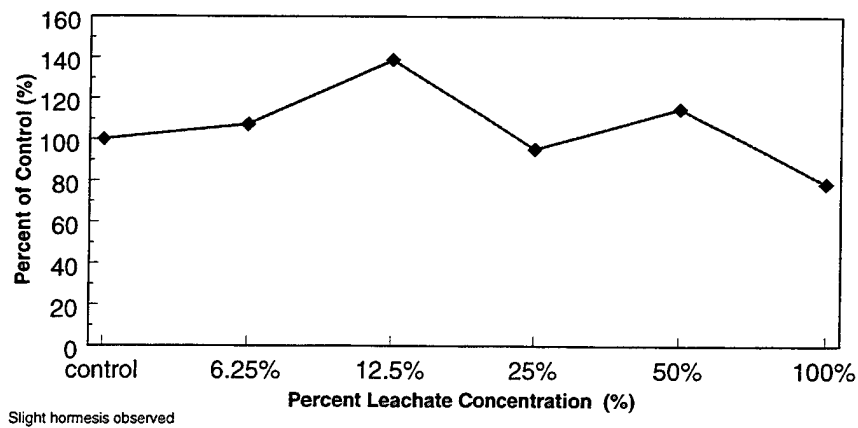


**Figure 6. TDU 14 - 100% Leachate Outside Canister**

***Gonyaulax polyedra***

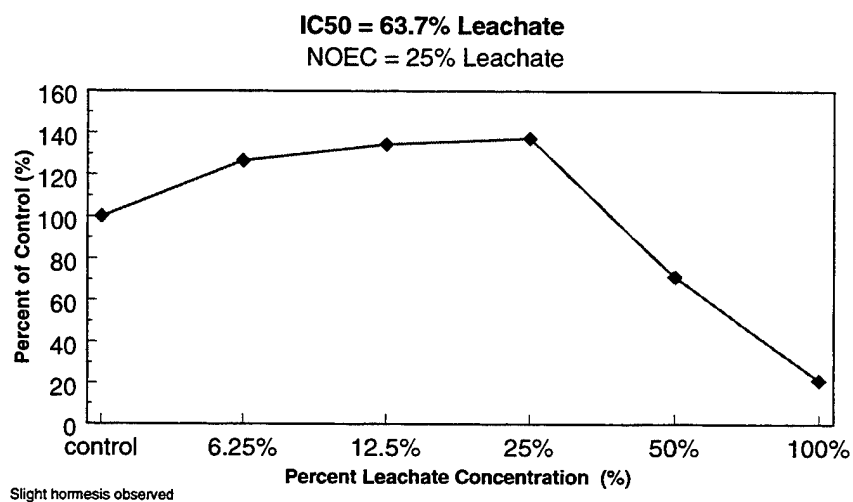
IC50 not found

NOEC > 100% Leachate



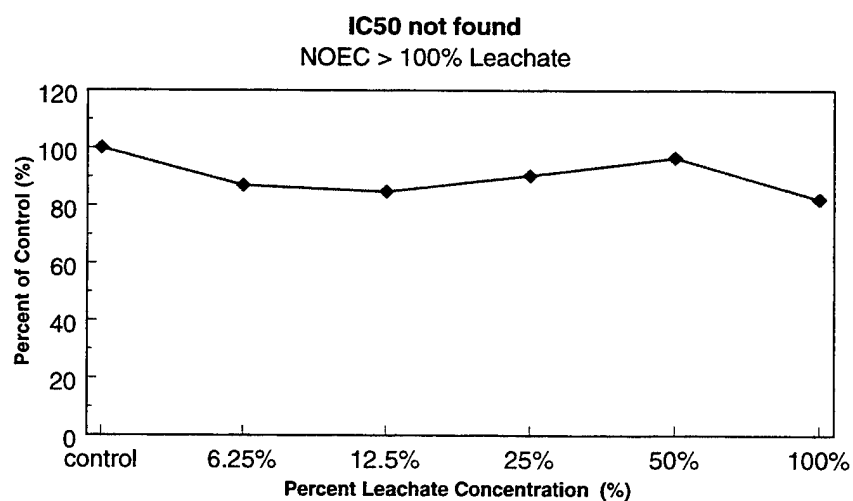
**Figure 7. TDU 17 - 100% Leachate Inside Canister**

*Gonyaulax polyedra*



**Figure 8. TDU 17 - 100% Leachate Outside Canister**

*Gonyaulax polyedra*



## **Appendix C**

### **TDU CORROSION STUDY**

Source: Wayne Glad  
Naval Command, Control, & Ocean Surveillance Center,  
RDTE Division Code D662

# CHEMICAL AND CORROSION ANALYSIS OF SUBMARINE TRASH DISPOSAL UNIT CANS

## Introduction

The Code 662 materials laboratory received, for characterization and analysis, a complete container used on submarines for the ejection of garbage. Also received were a second piece of material from a garbage container that appeared to be galvanized, and an iron weight that is put in the container with the garbage to ensure that it sinks to the bottom. The purpose of this characterization and analysis is to identify these materials and predict, using information from the corrosion literature, their corrosion rates in sea water under various conditions.

## Analysis Methods

The methods employed are Energy Dispersive X-ray Spectroscopy (EDS) in the Scanning Electron Microscope (SEM), Inductively Coupled Plasma (ICP) optical emission spectroscopy, combustion carbon-sulfur analysis, and optical metallography. EDS is used to quickly semi-quantitatively determine the composition of samples, and also examine surface features like coatings and corrosion products. The ICP is used to accurately determine the elemental composition of samples. Combustion carbon-sulfur analysis is the method most commonly used to determine carbon in steel (the ICP cannot determine carbon in steel accurately). Optical metallography is used here to make dimensional measurements of the sheet metal and coatings. It is also used to reveal the microstructure of the iron weight sample, which determines (along with the composition) the type of cast iron. These methods are discussed in more detail in enclosure 1 of Memo Ser 815/7 of 21 June 1995. Also used in the chemical analysis of the iron weight was spark emission spectroscopy. In spark emission spectroscopy a spark is struck between an electrode and a flat surface of the sample to be analyzed. Light from the spark contains atomic emission lines from the constituents of the sample. The light is dispersed by a grating and selected atomic emission lines are detected by photo-multiplier tubes. The detected signals are compared with signals from calibration standards to provide a quantitative analysis of the sample. When calibration standards are available and the sample geometry is favorable, spark emission is a faster analysis method than ICP, which requires dissolution of the sample.

## Results

### ***SEM-EDS Analysis (Gross elemental composition and coating analysis)***

While the complete container was expected to be mild steel sheet, the bright (lack of corrosion) condition of the container made us suspect that perhaps it was a stainless steel or had an enamel coating. A piece of the metal was cut from the complete container, washed with isopropyl alcohol and examined in the SEM. At 20 keV accelerating voltage the x-ray line from the iron in the steel was easily seen, indicating that if a coating was present it was quite thin. No nickel or chromium was detected, so the sheet was not a stainless steel. Spectra were taken at 5 keV accelerating voltage to see if a thin coating could be detected. Spectra are shown in Figure 1.

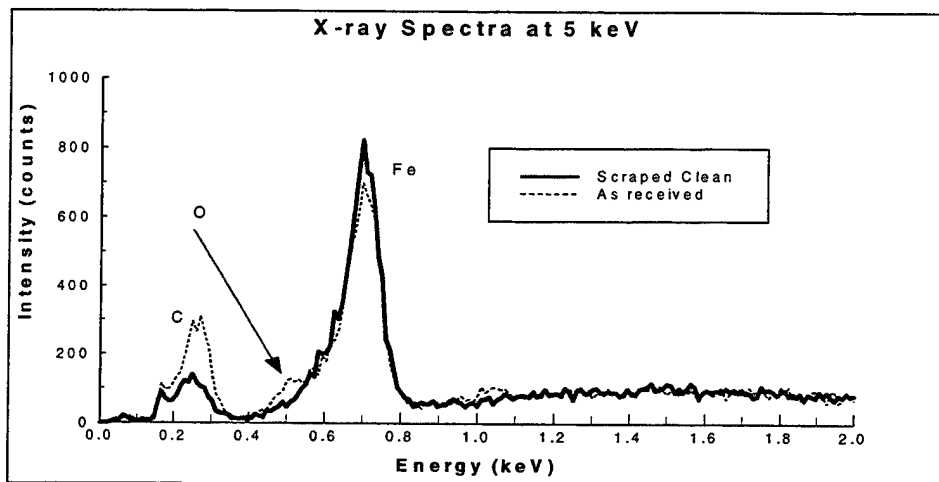


Figure 1. X-ray spectra from sheet surface.

The "as received" surface showed the presence of carbon and oxygen in the x-ray spectrum that was not present in an area that had been scraped with a knife. There probably is a coating present that contains carbon and oxygen, but it is sub-micron in thickness (not an enamel). The coating may only be a processing oil that incidentally provides some atmospheric corrosion protection. This coating would not be expected to provide much corrosion protection in sea water.

### ***Carbon-Sulfur Analysis (Carbon and Sulfur content of steels)***

Pieces of metal were cut from the top, bottom and body of the complete container. Pieces were also cut from the galvanized sample, and the zinc coating was removed by immersion in 6M hydrochloric acid. A small piece was also cut from the iron weight. The results of the analyses are shown in Table 1.

**Table 1 Carbon/ Sulfur Analysis Results**  
(Results in percent by weight)

Sample	Carbon	Sulfur
Body #1	0.0732	0.0126
Body #2	0.0716	0.0131
Bottom #1	0.0745	0.0131
Bottom #2	0.0802	0.0128
Top #1	0.0794	0.0127
Top #2	0.0795	0.0129
Top #3	0.0832	0.0129
<b>Average</b>	<b>0.077</b>	<b>0.013</b>
<b>Average for galvanized</b>	<b>0.111</b>	<b>0.015</b>
<b>Average for iron weight</b>	<b>3.28</b>	<b>0.088</b>

### ***ICP Analysis (Alloying elements in steel)***

Samples of about 0.5 gram mass were weighed, dissolved in nitric and hydrochloric acids and diluted to 100.0 ml. The liquid samples were then analyzed with the ICP spectrometer. The results of the analysis are given in Table 2 below. The galvanized sheet had an average zinc composition of 7.65 % by weight. The concentrations stated in table 2 for the galvanized material refer to the steel part of the sheet only.

**Table 2 ICP Analysis Results**  
(Results in percent by weight. Iron is remainder)

Sample	Co	Cr	Cu	Mo	Ni	P	V	Ti	Si	Mn
Body	0.102	0.011	0.003	0.00	0.017	0.002	0.003	0.00	0.00	0.20
Bottom	0.108	0.011	0.003	0.00	0.017	0.00	0.002	0.00	0.00	0.20
Top	0.066	0.013	0.004	0.00	0.016	0.00	0.00	0.00	0.00	0.20
Average Galvanized	0.166	0.025	0.009	0.00	0.087	0.009	0.004	0.000	0.032	0.37

### ***Spark Emission Spectroscopy (Alloying elements in cast iron)***

The composition of the iron weight was determined using spark emission spectroscopy. This is preferable to using ICP for this sample because of the presence of insoluble silicon in many cast irons. A sample about 1 inch by  $\frac{3}{4}$  inch by  $\frac{3}{4}$  inch was cut from the weight. One side of the sample was ground flat with 60 grit aluminum oxide paper. The sample was then sparked in the emission spectrometer, which was calibrated using gray iron standards from the Brammer Standard Company. The analysis results are shown in Table 3.

**Table 3 Elemental Composition of Cast Iron Weight**  
(Results in percent by weight. Iron is remainder)

Element	Concentration
Mn	0.57
P	0.08
Si	2.40
Cu	0.48
Ni	0.013
Cr	0.064
Mo	0.030
Sn	0.004
Ti	0.019
C (from combustion analysis)	3.28

### ***Optical Metallography (Dimensional measurements and iron microstructure)***

Samples of the container and weight material were mounted, ground and polished. Samples were also etched with nital (a mixture of nitric acid and ethanol) to make the microstructure visible and to remove smeared zinc from the galvanized sample. Figure 1 is a cross section of the galvanized sheet. The total thickness of the sheet is between 0.018 and 0.019 inch. Figure 1 is a cross section of the trash disposal unit galvanized sheet at higher magnification. The thickness of the coating is measured on this micrograph to be between 0.0008 and 0.0009 inch.

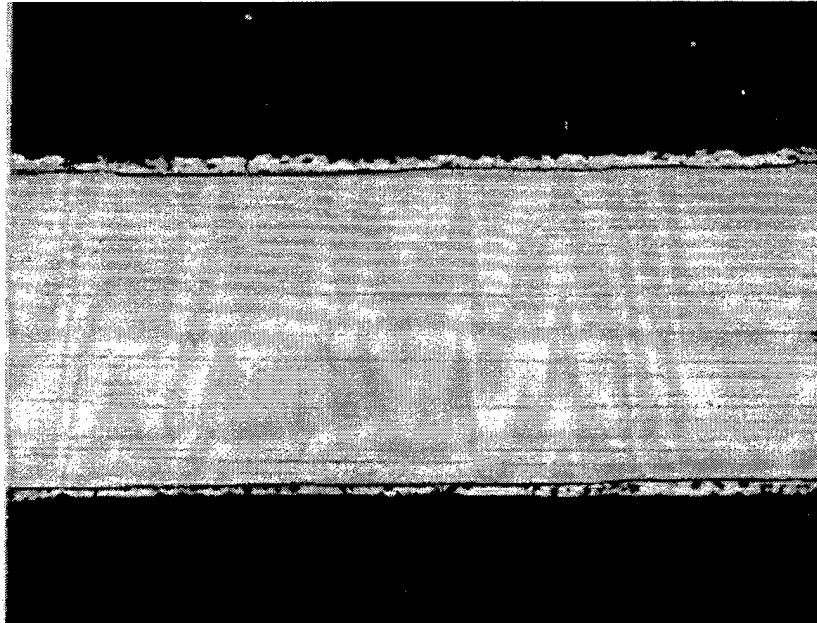


Figure 2. 100 X. Galvanized sheet cross-section. Etched with 9% nital.

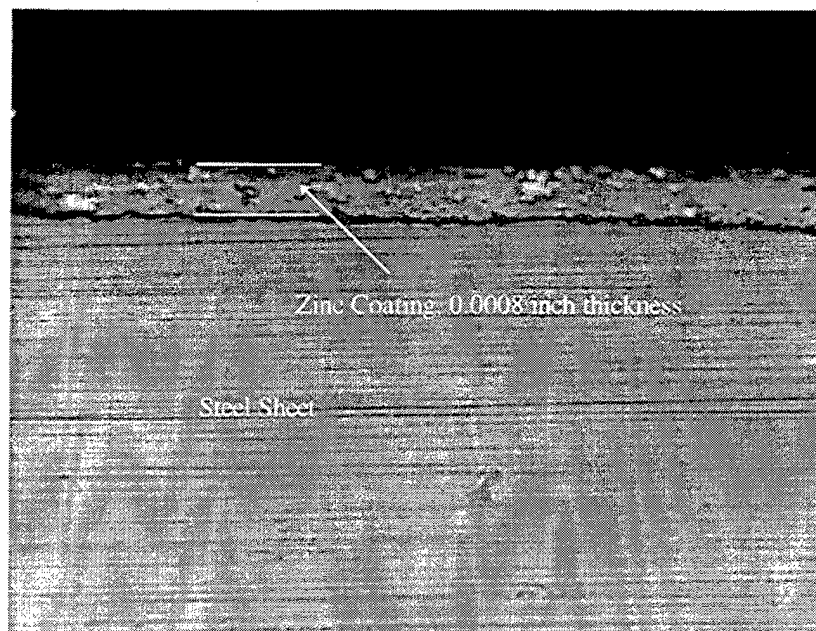


Figure 3. 400 X. Galvanized sheet etched with 9% nital.

Figure 3 is a cross section from the body of the complete container. The container top, bottom and body all had thicknesses of 0.020 inch, which were measured from micrographs. There was no coating detectable by optical microscopy. Figure 3 is a cross section of the iron weight. This micrograph shows the presence of graphite flakes and pearlite that is characteristic of gray cast iron.

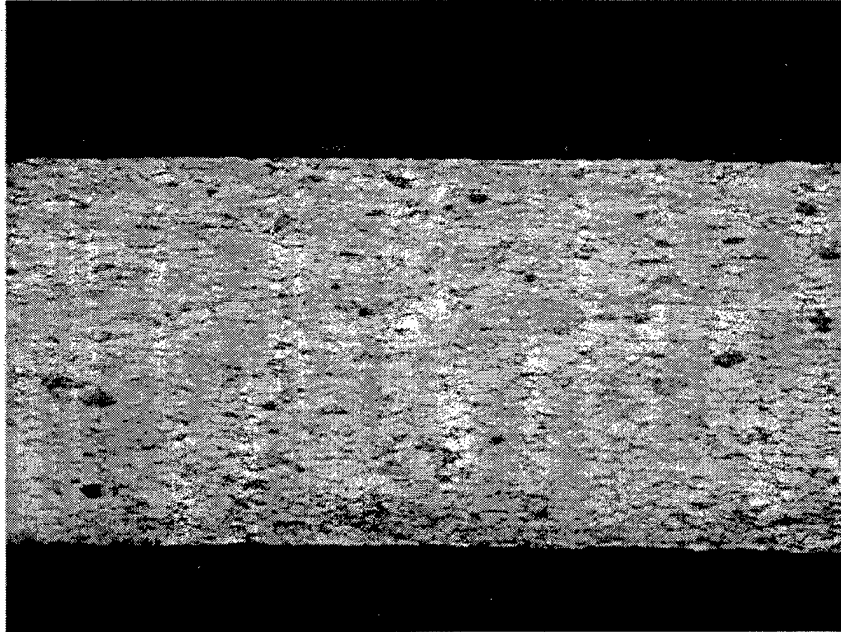


Figure 4. 100 X. Cross section of container body. Etched with 9% nital.

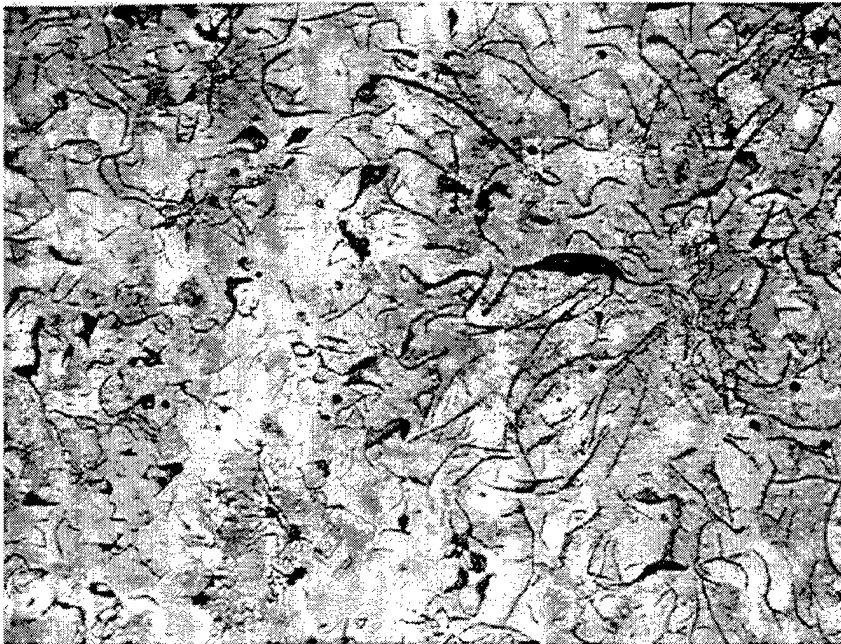


Figure 5. 100 X. Cross section of iron weight. Etched with 9% nital.



## Discussion

### *Complete container*

The complete submarine garbage container appears to be type 1008 rolled sheet steel. The thickness of the sheet is 0.020 inch. While information from NAVSEA indicates that the containers should be made from 1020 steel, we are not surprised that the analysis indicates that it is 1008. Because of fabrication and cost constraints the vast majority of steel sheet is made from steel with a carbon content less than 0.15% by weight. Type 1020 steel has a carbon content of 0.18-0.23 %. The sheet may have a very thin organic coating that helps preserve its bright finish. Any such coating would not have an effect on the corrosion rate of the material in sea water.

Table 4 gives corrosion test data<sup>1</sup> for 1010 steel (1008 steel would be expected to perform similarly to 1010). At deeper ocean depths the corrosion rates are about 1-2 mils per year (mpy). Since corrosion can take place both on the inside and outside of the container, a 0.020 inch thick container would be expected to last about 5 years at a 2 mpy corrosion rate. Based on the area of a container (neglecting the holes), a single garbage container would contribute about 400 grams of corroded steel per year to the marine environment at the 2 mpy corrosion rate.

**Table 4 Corrosion Rates for AISI 1010 Steel (from Reinhart<sup>1</sup>)**

Depth (ft.)	O <sub>2</sub> Concentration (ml/l)	pH	Salinity (ppt)	Temperature °C	Exposure time (days)	Rate Exposed (mpy)	Rate Buried (mpy)
5	5.9	8.1	33.51	15	181	9.1	-
5	5.9	8.1	33.51	15	366	8.0	-
5	5.5	8.1	33.31	15	588	8.9	-
2340	0.4	7.5	34.36	5	197	1.6	1.2
2370	0.4	7.5	34.36	5	402	1.1	1.1
5640	1.3	7.6	34.51	2.3	123	2.7	1.9
5640	1.3	7.6	34.51	2.3	751	0.8	0.6
5300	1.2	7.5	34.51	2.6	1064	1.0	0.7
6780	1.6	7.7	34.40	2.2	403	1.9	1.1

<sup>1</sup> Reinhart, F. M. "Corrosion of Metals and Alloys in the Deep Ocean", Technical Report R 834, Civil Engineering Laboratory, Naval Construction Battalion Center, Port Hueneme, California 93043, February 1976.

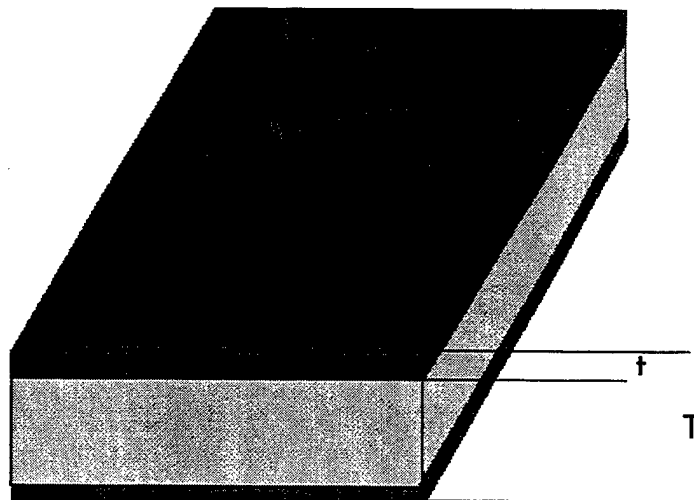
## Galvanized Material

The galvanized material had a slightly higher carbon content than the complete container, and is probably type 1010 steel. Optical metallography shows the thickness of the galvanized coating to be about 0.0008-0.0009 inch. The thickness of the sheet was between 0.018 and 0.019 inch. Because the thickness of zinc coatings of this type can vary somewhat over a part (as can be seen in figure 2), a single optical measurement is not always the best measurement of the average coating thickness. The average coating thickness can also be calculated from the zinc concentrations measured during the ICP analysis. This has the advantage of providing a thickness measurement that may better reflect the average coating thickness and is independent of the optical method. The calculation is done in the following manner:

A schematic of a piece of sheet metal that is plated on both sides is shown in the diagram at the right. If the coating thickness is  $t$  and the total thickness is  $T$ , then using the relations between the masses, volumes, area,  $A$ , and densities gives the following system of equations:

$$t = \frac{m_{Zn}}{2\rho_{Zn}A} \quad (1)$$

$$T - 2t = \frac{m_{Fe}}{\rho_{Fe}A} \quad (2)$$



that can be solved for  $t$  (eliminating  $A$ ) yielding:

$$t = \frac{m_{Zn}T\rho_{Fe}}{2(m_{Zn}\rho_{Fe} + m_{Fe}\rho_{Zn})} \quad (3)$$

where  $m_{Zn}$  is the mass of zinc in the sample determined from the ICP measurement,  $m_{Fe}$  is the mass of iron determined from weighing the sample and subtracting the mass of the zinc, and  $\rho_{Zn}$  and  $\rho_{Fe}$  are the densities of zinc and iron respectively. The distance  $T$  was measured with a micrometer to be 0.019 inch. We took  $\rho_{Zn}$  to be 7.14 gram/cm<sup>3</sup> and  $\rho_{Fe}$  to be 7.833 gram/cm<sup>3</sup> (the density of 1010 steel). The results of measurements on three samples of the galvanized material is shown in table 5.

**Table 5 Measured masses, concentrations, and calculated coating thicknesses for galvanized material**

Sample masses (grams)	Percentage Zinc	Calculated Thickness (inch)
0.521	7.5	0.00078
0.473	7.8	0.00081
0.535	7.6	0.00078

Reinhart<sup>1</sup> exposed galvanized sheet steel (zinc coating thickness 0.017 inch) at a depth of 2370 feet. He found that that coating protected the steel from corrosion for 3-4 months. Since the coating observed on the galvanized sheet examined here is about half that thickness, the protection would be expected to last about half as long, 1.5-2 months. This is a negligible amount of time compared with the actual lifetime of the 1010 steel container in sea-water, which would be the same as the non-galvanized container, about 5 years.

### **Trash Disposal Unit Weight**

Based on the chemistry and metallography results, the trash disposal unit weight material is a gray cast iron, probably an SAE grade G2500. Gray cast iron is an inexpensive material that is well suited for its use here as a weight. Table 6 shows the corrosion rates for gray cast iron under a variety of conditions. The corrosion resistance of the cast iron is somewhat greater than that of steel at higher dissolved oxygen content, but is very similar at the lower oxygen levels. The cast iron weight, which is about ¾ inch thick, would last 188 years at a 2 mpy corrosion rate. This result is obtained simply by dividing the smallest dimension of the weight disk (the .75 inch thickness) by the 4 mpy corrosion rate that would result from corrosion of each side of the disk. The mass loading from the weight would be initially about 24 grams per year. The rate would slow to about 16 grams per year near the end of the 188 year lifetime of the weight due to the decrease in the surface area of the weight.

an

**Table 6 Corrosion Rates for Gray Cast iron (from Reinhart<sup>1</sup>)**

Depth (ft)	O <sub>2</sub> Concentration (ml/l)	pH	Salinity (ppt)	Temperature °C	Exposure time (days)	Rate Exposed (mpy)	Rate Buried (mpy)
5	5.9	8.1	33.51	15	366	2.6	-
2340	0.4	7.5	34.36	5	197	2.0	0.3
2370	0.4	7.5	34.36	5	402	1.7	2.0
5640	1.3	7.6	34.51	2.3	123	4.2	3.0
5640	1.3	7.6	34.51	2.3	751	1.2	1.0
5300	1.2	7.5	34.51	2.6	1064	0.8	0.5
6780	1.6	7.7	34.40	2.2	403	1.8	1.3

### **Summary**

**1. Complete Container.** A complete trash disposal unit was examined and found to be constructed of 1008 steel sheet of 0.020 inch thickness. There may be a very thin oil-like coating on the sheet that would have no effect on its corrosion behavior in sea water. This type of steel will corrode at a rate of about 2 mils per year at deep ocean depths. A container would have a lifetime of about 5 years under these conditions. The container would contribute about 400 grams of material per year to the ocean environment.

**2. Galvanized material.** Some galvanized material from which trash disposal units have been constructed was examined and found to be constructed of 1010 steel sheet of .018 inch thickness. The sheet had a galvanized coating of about 0.0008 inch on each side. The zinc coating amounts to 7.65% of the mass of the sheet. In sea water a galvanized coating of this thickness would only

last about 1.5-2 months. The lifetime of a container made from galvanized sheet would be about the same as that of ungalvanized sheet.

**3. Weight.** A weight that is added to a container of trash to ensure that it sinks to the bottom of the ocean was examined. It was made of gray cast iron. Gray cast iron has somewhat better corrosion resistance than 1010 steel does in sea water at high oxygen concentrations, but at depths where the oxygen concentration is smaller the corrosion rate is comparable to 1010 steel, about 2 mils per year. A weight would last about 188 years in deep sea water before corroding completely away. The weight would initially contribute about 24 grams of material to the environment each year. Near the end of its lifetime in sea water the weight would contribute about 16 grams per year due to the reduction of its surface area over time.

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